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USE OF FLUE GAS DESULFURIZATION GYPSUM FOR THE REMOVAL OF OFF-FLAVOR COMPOUNDS IN FISH POND WATER

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ABSTRACT: Accumulation of off-flavor in fish flesh caused by the presence of geosmin and 2-methylisoborneol (MIB) in pond waters is a worldwide quality problem in aquaculture. This study investigated the effectiveness of synthetic flue gas desulfurization gypsum, (FGDG) a cheap and readily soluble material from coal-fired electric utilities, for the removal of off flavor substances: geosmin and MIB, in fish pond water. Water samples from fish ponds were spiked with known concentrations of geosmin and MIB and varying amounts of FGDG (0, 200, 400 and 600 mg/L) were added to compare the removal rates of geosmin and MIB, chlorophyll *a* levels and orthophosphate. The experiment was conducted for 9 days. It was revealed that FGDG had significantly reduced both geosmin and MIB in spiked pond waters when compared with the control (0 mg/L) ($P<0.05$). The highest removal rate of geosmin (63.41%) was found when 600 mg/L of CFG was used after 9 days. However, the removal rate of geosmin at 200 and 400 mg/L FGDG was not significantly ($P>0.05$) different from 600 mg/L. The highest removal rate of MIB (75.63%) was found with the treatment with 400 mg/L CFG after 6 days. In addition, 200 mg/L FGDG was also highly effective in reducing chlorophyll *a* and orthophosphate concentration through calcium phosphate precipitation. It was suggested that 200 mg/L FGDG is the suitable dose to apply for the removal of off-flavor compounds in fish pond waters.

Keywords: Off-flavor, Removal, Gypsum, Geosmin, MIB

INTRODUCTION

Increase in population resulting in increased demand has pushed extensive aquaculture towards intensively operated production systems and commonly resulting in eutrophic conditions and cyanobacterial blooms. Cyanobacterial secondary metabolites can cause undesirable tastes and odors leading to acceptability issues in aquaculture products [1], [2]. Off-flavors especially earthy-musty off-flavors in drinking water supplies and aquatic animals for human consumption are world-wide problems. 2-methylisoborneol (MIB) and geosmin are the two most common earthy/musty-causing compounds. These off-flavors metabolites can be detected by consumers at the concentrations as low as 5–10 ng/L [3]. Some studies have shown that earthy/musty aromas were excreted by cyanobacteria such as *Anabaena* sp., *Oscillatoria* sp., *Lyngbya* sp. [4]-[6]. The conventional methods for controlling cyanobacterial bloom (sources of metabolites) are coagulation, clarification, filtration, algaecide and ozone [7], [8]. These methods, except coagulation, are usually expensive, complicated and can cause further pollution due to the use of chemicals.

Synthetic gypsum from flue gas desulfurization or flue gas desulfurization gypsum (FGDG) is a pure form of gypsum ($CaSO_4 \cdot 2H_2O$) that is a by-product from the combustion of coal for energy production. FGDG is chemically similar to commercial or mined gypsum and has been used in agriculture as a beneficial soil amendment and as nutrient source for all crops. It is a cheap and readily available source of calcium and sulfur that has been widely used not only in agriculture for recovery of alkali soils and as a source of calcium and sulfate in fertilizer [9]-[11] but also for production of interior construction materials and as a filler ingredient in some food and toothpaste. Some studies suggested that natural rock gypsum powder could be used as a pond treatment in aquaculture for: flocculation of clay particles, increasing the concentration of calcium and total hardness, precipitation of phosphate and reducing in water pH [12]. However, information on using FGDG for water treatment in aquaculture especially in algal-rich ponds is limited and no data exist showing the effects of treatment on incidence of off-flavor. Therefore, this study aimed to evaluate the effectiveness of FGDG in removing off-flavor compounds in pond water. Effects of FGDG in phytoplankton cells and in water quality were also studied.

MATERIALS AND METHODS

Experimental Protocol

Algal-rich water samples collected from fish ponds were spiked with known concentrations of geosmin and MIB 5 μg/L and added with varying amounts of FGDG (0, 200, 400 and 600 mg/L). Three replications of each group were performed. Synthetic flue gas desulfurization gypsum used in this study was purchased from a local company in Lumpang, Thailand.

The removal rate of geosmin and MIB, chlorophyll a levels and water quality were monitored for 9 days. The production of hardness of each concentration was analyzed to compare with the analytical grade gypsum.

Analysis of Geosmin and MIB in Water

Off-flavor extraction from water was conducted by headspace solid phase microextraction (HS-SPME) and analysis by gas chromatography-mass spectrometry (GC/MS) (Agilent Technology, USA) [13]. Geosmin and MIB standards were obtained from Sigma-Aldrich Corporation, USA and were used in spiking the pond water samples.

Water Quality and Nutrient Analysis

Standard methods [14] were used for the analysis of total hardness, and orthophosphate-phosphorus in the laboratory.

Hydro-biological Analysis

Chlorophyll *a* in the water samples was extracted with 10 mL of hot methanol (60ºC in water bath) and quantified with a spectrometer (Hach DR4000, USA) [14]. Chlorophyll *a* concentration was calculated as described by Wintermans and de Mots [15] and Saijo [16].

Data Analysis

Analysis of variance (ANOVA) was used to test for difference between means of observed parameters in each treatment. Duncan Multiple Range Test (DMRT) at 95% confidence level was used for treatment comparison. T-test was used to compare means of two groups.

RESULTS AND DISCUSSION

1. Effect of gypsum on total hardness

The two gypsum materials (analytical grade gypsum and FGDG) gave different concentrations of total hardness (Fig. 1). The analytical grade gypsum showed higher total hardness than the FGDG due to its very high purity. A positive correlation between total hardness and gypsum concentration in both materials was established the total hardness per 1 mg of the analytical grade gypsum and FGDG was 0.546 and 0.329 mg/L of $CaCO_3$, respectively (Fig. 2). In this study, FGDG dissolved easily and provide hardness to the water. Some studies reported that gypsum is more soluble than the liming materials used in aquaculture and has been widely used for increasing concentration of calcium and total hardness [11], [12] in fish pond water. FGDG, being a cheap and readily-available material, is therefore suggested as a source of hardness in water for aquaculture. Table 1 shows the composition of the FGDG used in the study consisting of two major components, which are CaO (37.19 %) and SO_3 (50.32 %). Therefore, this raw material consists nearly to 100% of calcium sulfate hydrate which contribute to the permanent hardness of pond water. Additional physico-chemical properties of FGDG determined include: color (light brown), specific gravity (2.23 g/cm^3) and pH (7.3) [19].

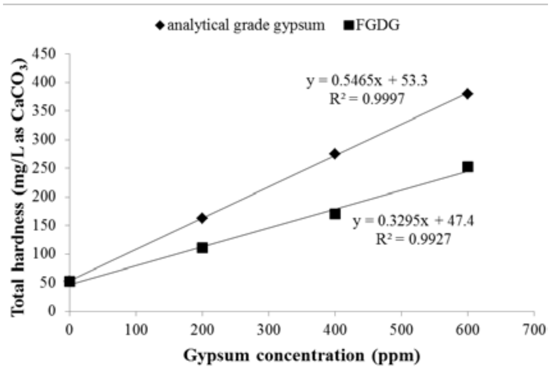

Fig. 1 Relation between total hardness and gypsum concentration

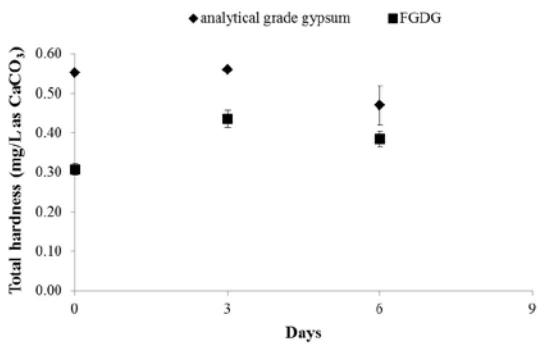

Fig. 2 Total hardness concentration for 1 mg/L analytical grade gypsum and FGDG

2. Effect of FGDG on geosmin and MIB removal in fish pond water

FGDG could reduce both geosmin and MIB in pond water when compared with the control (0 mg/L). Geosmin level was reduced from 3 days onwards when treated with different concentrations of FGDG (Fig. 3a). The highest removal rate of geosmin (63.41%) was observed in the treatment using 600 mg/L FGDG (Table 2). However, removal rates of geosmin in both 400 and 200 mg/L FGDG were not significantly different from 600 mg/L (Fig. 3b-c, Table 3). This comparability could be due to the solubility of varying gypsum concentrations in water. According to Wu and Boyd, the solubility of calcium sulfate (in pond water) at concentrations of 50-1,600 mg/L at 25°C ranged from 88.6 to 95% and that dissolution increased with decreasing concentration and with increasing temperature [11]. In addition, it was also found that the intracellular forms of both compounds showed better removal rate than the dissolved forms of geosmin and MIB. It could be that the negative charge that the cyanobacterial cells carry was countered in the presence of FGDG. The positively-charged FGDG interact with the negatively-charged cyanobacterial surfaces, bind them and settled [20].

MIB concentration in pond water decreased slightly after 3 days (Figure. 3d) but removal rates showed a sharp decrease after 6 days when treated with FGDG (Fig. 3e-f). The highest removal rate of MIB (75.63%) was attained at 400 mg/L FGDG (Table 2).

Table 1 Chemical composition of FGDG from Mae Moh power plant, Lampang province, Thailand [19].

Compound	Weight %
SiO_2	1.96
Al_2O_3	0.68
Fe_2O_3	0.35
CaO	37.19
SO_3	50.32
K_2O	0.04
TiO_2	0.12
MgO	0.73
P_2O_5	0.07
SiO_2	1.66
LOI*	8.81

**LOI = loss on ignition*

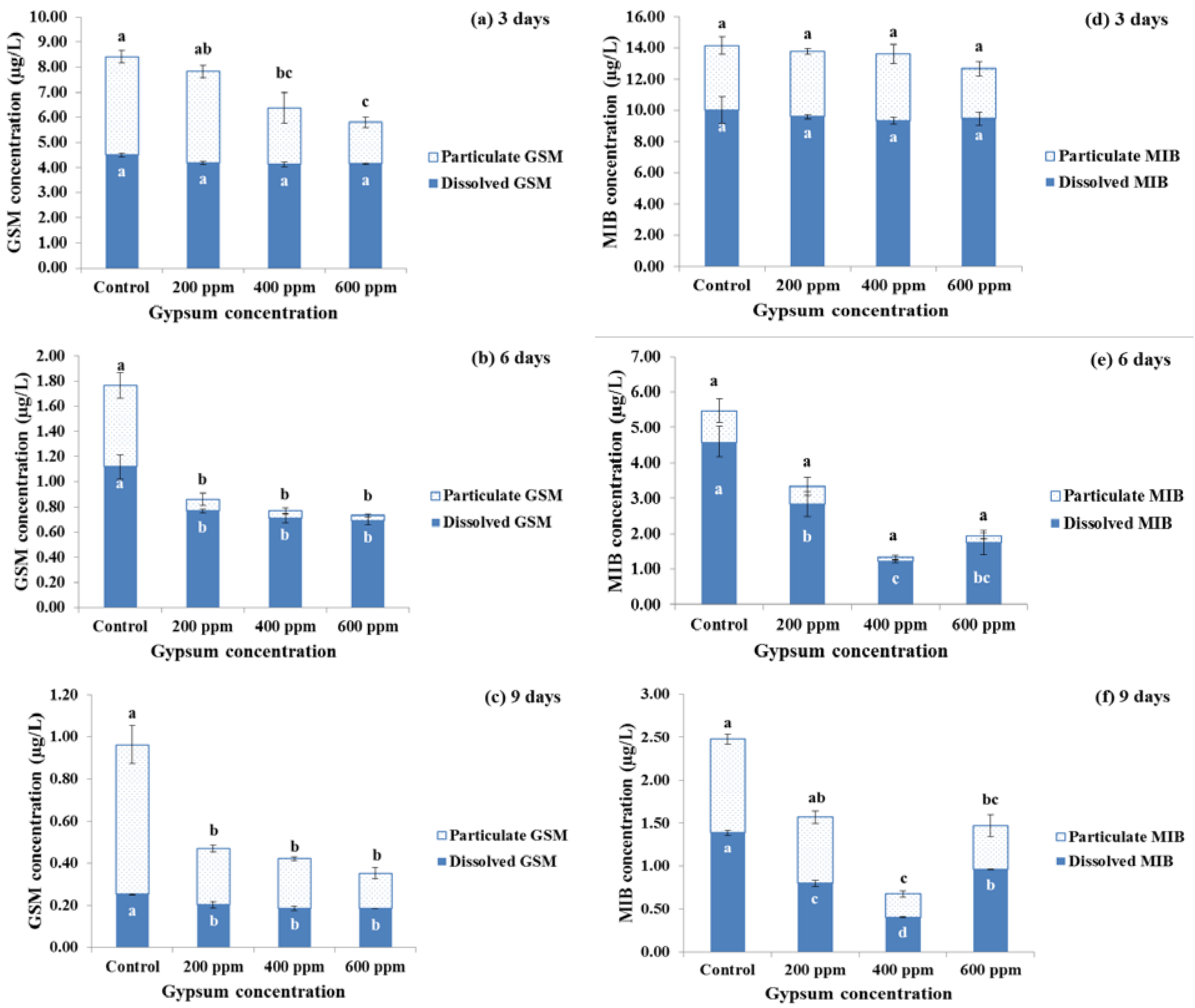

Fig. 3 Effect of FGDG on particulate and dissolved geosmin (a-c) and MIB (d-e) concentrations as a function of time

Table 2 Removal rate (%) of total geosmin and MIB at different FGDG concentrations

Days	Removal rate (%)					
	Total geosmin			Total MIB		
	200 mg/L	400 mg/L	600 mg/L	200 mg/L	400 mg/L	600 mg/L
3	6.92	24.25	31.11	2.62	3.89	10.43
6	51.32	56.50	58.47	39.15	75.63	64.64
9	51.14	56.14	63.41	36.67	72.68	40.79

Table 3 Effectiveness of FGDG in removing off-flavor compounds (geosmin and MIB) (mean ±SD)

FGDG (mg/L)	Off-flavor removal efficiency (ng/mg FGDG)	
	Geosmin	MIB
200	3.30 ± 0.63	5.71 ± 2.63
400	2.98 ± 1.11	5.42 ± 2.64
600	2.37 ± 1.02	3.35 ± 1.30

In general some filamentous cyanobacteria and actinomycetes released geosmin and MIB to the water. When algal die and decompose, these metabolites consisted both particulate and dissolved forms and have been shown to be somewhat recalcitrant to conventional water treatment [17], [18].

Based on this study, FGDG could be used for off-flavor removal in fish pond. The recommendation level is 200 mg/L

3. Effect of FGDG on chlorophyll *a* concentration

Increase of cyanobacterial biomass and the release of their secondary metabolites, including geosmin and MIB, present an enormous problem to fish and water quality in ponds. Chlorophyll *a* is generally considered as an important indicator of algal biomass [21].

In this study, the application of FGDG to reduce algal biomass was evaluated in the laboratory. It was shown that FGDG concentrations at 200, 400 and 600 mg/L could reduce the pond water's chlorophyll *a* level relative to the control treatment (Table 4). The highest efficiency of 1 mg/L FGDG that could reduce chlorophyll *a* was obtained in the treatment using 200 mg/L FGDG (Table 4). The reduction of chlorophyll *a* occurred via coagulation mechanism. Coagulation is a key step in conventional drinking water treatment for algal removal through colloidal charge neutralization followed by aggregation into floc [8]. In general, the effectiveness of coagulants increases with the charge on the metal ion. The calcium (Ca^{2+}) in gypsum is more effective because it carries a +2 charge [22]. Wu and Boyd [11] also reported that treatment of ponds at Auburn University with 250-500 mg/L of agricultural gypsum affected turbidity: many substances suspended in water including phytoplankton. Removal is similar to that achieved with 15-25 mg/L alum but gypsum has the advantage of a longer residual life than alum, and it is safer to use. Another possible mechanism of gypsum treatment is the reduction of phytoplankton abundance by lowering dissolved orthophosphate concentration through calcium phosphate precipitation in water. [11].

Table 4 Reduction of chlorophyll *a* at varying FGDG concentrations

FGDG (mg/L)	Reduction efficiency of chlorophyll *a* (µg chlorophyll *a*/ mg FGDG)
200	1.26
400	1.16
600	0.74

4. Effectiveness of FGDG on orthophosphate removal

Phosphorus is an essential phytoplankton nutrient. In the commercial fish culture most phosphate gets into the water from metabolic waste of fish and from decomposition of uneaten feed [6], [23]. As feeding rate increases, nutrient concentration rises then the phytoplankton become more abundant.

In this experiment, the effect of FGDG on dissolved orthophosphate concentration was investigated. The FGDG-treated water showed higher reduction in orthophosphate concentration than in the control group (Figs. 4 and 5). The highest effect of FGDG that could reduce orthophosphate concentration was observed in the treatment using 600 mg/L FGDG after 9 days. However, the removal rates of orthophosphate at 200 and 400 mg/L FGDG were not significantly different (P>0.05) from the 600 mg/L –treated water.

Expectedly, FGDG treatment reduced the orthophosphate concentration in pond water through calcium phosphate precipitation. Wu and Boyd [11] reported that in aquaculture ponds with low calcium concentration, gypsum application would dramatically reduces soluble reactive phosphorus and total phosphorus concentrations by phosphate precipitation. Additionally, gypsum is safe for human and aquatic life; its residual time in the pond depends on water flocculant retention time meaning it is slowly lost from pond waters and influence phosphorus levels for a longer period of time than alum treatment. Therefore, FGDG is a suitable material for use in aquaculture ponds.

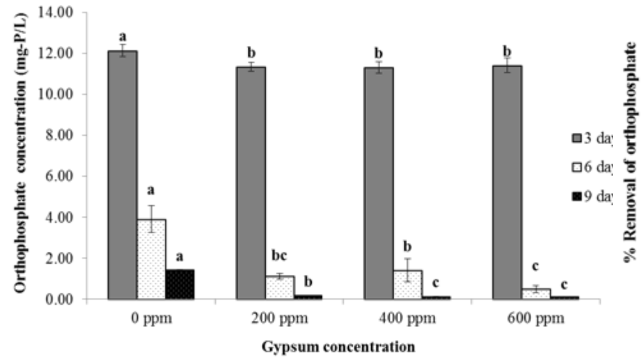

Fig. 4 Orthophosphate concentration in fish pond water

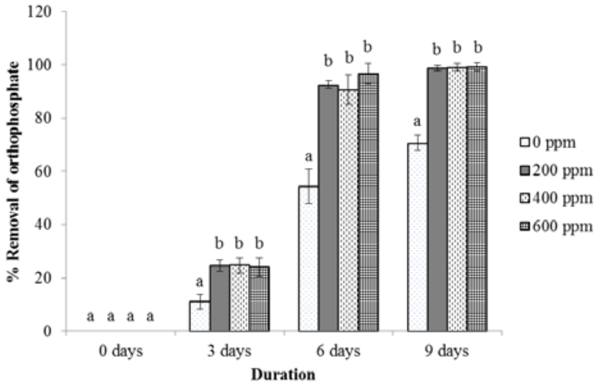

Fig. 5 Removal rate of orthophosphate at varying FGDG concentrations

CONCLUSION

It was confirmed that FGDG at 200 mg/L was suitable for the reduction of geosmin and MIB levels especially for the particulate form. It also reduced phytoplankton in algal-rich pond water because it was shown to be effective in reducing chlorophyll *a* In addition, FGDG could also remove orthophosphate in fish ponds water through calcium phosphate precipitation which is an alternative way to control the problem from phytoplankton in fish culture. Finally, it was recommended that FGDG can be used for water quality improvement in an aquaculture pond.

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