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# Evaluation of Mechanical Methods Used for The Enhancement of Dissolved Oxygen And Removal of Ammonia Toxicity From Intensive Shrimp Farming Wastewater

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## Abstract

*Ammonia ($NH_3$) is produced in shrimp culture wastewater and potentially toxic to aquatic animals especially in low dissolved oxygen (DO) conditions. Therefore the enhancement of DO levelsand$NH_3$toxicity removal is important in tertiary wastewater treatment and is necessary to bring $NH_3$to a safer level to achievebiological treatmentof shrimp effluents. The performance of five mechanical treatment methods used in aquaculture including splash board, gutter, diffuse aerator system, paddlewheel anda porcupine-fan wereevaluated in terms of their efficiency in the treatment of shrimp wastewater for enhancement of DOand removal of $NH_3$from shrimp farming wastewater. The experiments were conducted at the last month of the shrimp crop production cycle. Results indicated that these five treatment methodshave potentialin increasing DO and removing$NH_3$toxicity. However, among all instruments,the splash board method was found to be more efficientthan the other treatment methodsin terms of treatment performance and less energy requirement. Splash board produced the highest increase in DO(6.64 mg $L^{-1}$) and followed by gutter (4.65 mg $L^{-1}$) treatment within the six hours. The value of DO was comparatively lower in other methods such asporcupine-fan (3.91 mg $L^{-1}$)>paddlewheel (3.78 mg $L^{-1}$)>diffuse aerator system (3.2 mg $L^{-1}$)and control (0.88 mg $L^{-1}$)during the same period. Ammonia removal by splash board was up to 99.3% within six hours, followed in order bygutter (76.8%), porcupine-fan (63.6%), paddlewheel (55.0%) and diffuse aerator system (44.4%) while the $NH_3$ levels increased in the control by up to 157.7% compared to the initial value.*

**Keywords**: oxygen, ammonia toxicity, shrimp effluent, wastewater treatment, intensive shrimpculture

## Introduction

Dissolved oxygen (DO) is one of the important environmental parameters that exerts great effects on growth and production of aquatic animals in general andshrimpin particular. It has a direct effect on feed consumption and metabolism of animals but has indirect effects on the environment. As DO levels decrease, the shrimp may not have enough energy to swim and feed (Merkens and Downing, 2008). Shimoda et al. (2006) indicated that the survival, production and feed conversion ratio are directly impacted by DO levels in the pond which were improved in response to a higher DO threshold level. Therefore, several studies have focused on developing pond aeration systems to increase oxygen ($O_2$) supply. These aeration systems are modifications of standard wastewater aeration equipments such as paddlewheels, diffuser air systems and pump sprayers (Boyd, 1998). However, some of the commercial aerators are generally expensive to operate for aquaculture usage as they consume a significant amount of energy. In addition, these methods are primarily used in ponds for supplying $O_2$ or used as the aerator equipment in domestic wastewater treatment plants. These methods have not been evaluated in order to assess their capability to remove ammonia ($NH_3$)toxicity from shrimp wastewater, which plays an important role in shrimp survival and growth rate.

Ammonia is the most commonly occurring nitrogenous toxicity produced from intensive shrimp farmingwastewater. The removal of $NH_3$toxicity is an important part in tertiary wastewater treatment especially for integrated wastewater treatment systemsto meet water discharge standards. Ammonia is produced by shrimp's urine, feces excretion, and nitrogenous wastes but aremainly derived from high protein containing feed (Abeliovich and Azov, 1976; Gross et al., 2003; James, 2000). Ammoniacal nitrogen exists in two forms including unionized ammonia ($NH_3$) gas and ammonium ion ($NH_4^+$). The proportional amounts depend on pH and temperature and are described collectively as total ammonia nitrogen (TAN) (Jiang et al., 2004).

In wastewater, *Nitrosomonas* and *Nitrobacter*are two main chemoautotrophic bacteria that tend to oxidize ammonium ions ($NH_4^+$) to nitrite ($NO_2$) and nitrate ($NO_3$). Nevertheless, these ions are removed by aquatic plants, algae and bacteria since they assimilate them as a source of nitrogen (Jones et al., 2001). The $NH_3$ toxicity is excreted across the gill epithelium either by passive diffusion as $NH_3$gas because of gas partial pressure gradient between animal blood and water(Wilkie, 2002). The $NH_3$ must be eliminated from the body because it can become toxic whenit accumulates in aquatic animal body.

Techniques used for the enhancement of DO and removal of $NH_3$ toxicity include biological treatment, chemical precipitation, advanced oxidation process, membrane process or ion exchange. Boopathy et al. (2007) and Lyles et al. (2008) used an ion-exchange nitrification method through bacterial culturefor theremoval of $NH_3$ toxicity. However, this method did not respond well to a shock load of $NH_3$ and resulted in unacceptable peaks in effluent $NH_3$(Jorgensen and Weatherley, 2003).

Bernal and Lopez-Real (1993) and Huang et al. (2010) used clinoptilotile and natural synthetic zeolites for the removal of $NH_3$ by an ion exchangermechanism and reported that clinoptilotile and natural synthetic zeolites can be used to remove $NH_3$ from wastewater. However, thesemethods have limitations in removal performance and economic efficiency (Chiayvareesajja and Boyd, 1993). Krishnani(2002) used neemoil to achieve a higher reduction in $NH_3$ toxicity, but found that it hadlimitations, including the need for high $O_2$ levels and low temperature. Merdedes and Helgi (2008) and Mohamed and Daniel (2007) used ozone instead of $O_2$ or air to increase DO and $NH_3$ removal in wastewater, especially to clean or treat the water of the aquatic farms such as shrimp farm; however they consume more energy and are not suitable for open farm systems. In addition, these methods are expensive and complicated during operation, and hence are difficult for application in developing countries, particularly in small scale farming. Consequently, the simple methods such as water flow exchange by mechanical equipment are safe, friendly, cheap and easier to operate and are higher in $NH_3$ removal efficiency which are all necessary to aquaculture wastewater treatment.

Dissolved oxygen is an important factor for the removalof organic matter involving aquatic animals, while $NH_3$ has very significant effect on aquatic animal especially at low DO level and high pH and temperature. Therefore enhancement of DO levels and removal of $NH_3$toxicity arethe first stages in integrated wastewater system to manage pollutants from shrimp culture wastewater for further biological treatment using aquatic animals. This paperevaluatesthe efficiency of five different mechanical methods (splash board, gutter, diffused aerator system, paddlewheel, and porcupine-fan) particularly on the capacity to increase $O_2$ levels and remove toxic $NH_3$ gas from intensive shrimp farm wastewater. The principle of these methods is based on gas exchanges by facilitating water exposure to air during equipment operation. During the operation, $O_2$ from atmospheric air diffuses into the wastewater while the toxic $NH_3$ gas is removed to provide good conditions for biological treatment processesinvolving aquatic animals in subsequent stages of the integrated wastewater treatment system.

## Materialsand methods

***Equipments design and setup***

The equipments used to test the performance were setup based on their normal operations in a commercial intensive shrimpfarm operation. However, the structural parameters, particularly, the parameters such as hole size, hole density and slope of gutter and splash board were set up following the recommendations of recent studies byNguyen (2013).

The structure of the splash board consists of three parts: frame, three ladders and water supply system (Fig. 1a). The frame was made of wood (size 4 x 4 mm). Three ladders were also made of wood with the dimensions of 167 x 500 mm. The water supply system included vertical and horizontal pipes and a pump. The water pipes were polyvinyl chloride (PVC) pipes with a diameter of 21 mm. The vertical pipe connected the pump and horizontal pipe. The horizontal pipe had 50 holes (diameter of 0.2 mm), connected to the upper edge of the splashboard ladder and was located in the pond at five degrees.

Gutter was designed at optimal structural parameters including 12 mm for gutter diameter, 150 holes and 5 degree of slope. The gutter structure consists of three components: frame, gutter surface and a water supply system as shown in Fig. 1(b). The frame was made of v-shaped-steel (size 2 x 2 mm). The gutter surface was made of 0.25 $m^2$ stainless steel. The water was sieved through 150 (0.06 holes $cm^{-2}$) holes of gutter surface. The water supply system was similar to that used in the splash board system and includes pipes and a pump. The horizontal pipe had 50 holes (diameter 0.2 mm) and was connected to the upper edge of the gutter surface. Water from the gutter was sprayed over the sieved surface; hence $O_2$ concentration will be increased while toxic gases will be decreased.

Water was sprayed using the horizontal pipe over the ladders which flowed from the first ladder to the third ladder before moving on to the treatment tank surface. Water was supplied by a pump (Guangdong Risheng Group Co. Ltd Model Hx-2.4) with a water flow capacity up to 2800 $Lh^{-1}$ and 50W power through the PVC pipes.

Diffuser aerator systemconsisted of an air pump and pipes (Fig. 1c). This system used a low pressure (0.032 Mpa) pump but high volume air blower to provide air to diffusers positioned on the pond bottom. It was connected to a soft plastic pipe and then was connected to a PVC pipe (1000 mm length and 21 mm diameter). The PVC pipe had 100 bore holes (diameter of 0.2 mm) which were placed at the bottom of a 1 $m^3$ pond. Air from the pump was then diffused into the pond surroundings. The wastewater received air bubbles from an aerator system and then $O_2$was transferred from the bubbles to the surrounding water and the DO level was increased during aerator operation. Air was diffused by a pump (RESUN Group Co. Ltd. Model ACO-008A) with air capacity up to 115 $Lh^{-1}$ and 60W power. The pump dimensions were 260 x 162 x 175 $mm^3$.

The electric paddlewheel aerator used in this experiment consisted of a speed control motor and a paddlewheel mounted on a flotation device. This was the same design as Taiwan's paddlewheel aerator described by Boyd and Clay(1998) but was modified from the imported model manufactured by Truong Son Company, Vietnam. The major components of the paddlewheel design are: paddles, shaft and bearings (Fig. 1d). The dimensions of the paddlewheel are 5 cm diameter, 15 cm paddle depth and 60 cm shaft length. The paddlewheel shaft was fitted with bearings and mounted on a metal frame which was floated on a fixed steel bar. The paddlewheel was connected to the motor using roller bearings and placed at the end of the paddle shaft in polyurethane blocks. The paddlewheel was anchored on the frame above the water. The motor had a speed controller for the output shaft speed and the input speed of the paddle wheel and the speed ranged from 30 to 330 rpm. Motor power output was 250W and it was used for both paddlewheel and porcupine-fan design. In this experiment, the paddlewheel ran at 100 revolutions per minute (100 rpm).

The porcupine-fan was based on paddlewheel principles but the propellers were modified to improve the air supply (Fig. 1e). This porcupine-fan was also located on the surface of the pond. The dimensions of the fan propeller were 21 mm diameter, 15 cm depth and 60 cm shaft length. The propellers were made from PVC pipes and have improved design to reduce vibration, wear and power requirements, and also work durably compared to the simple paddlewheel aerator. Similarly to the paddlewheel, the porcupine-fan shaft was fitted with bearings and mounted on a metal frame which is floated with a steel bar. It was made of heat-resistant plastic pipe. It was connected to an electric motor by roller bearings and placed at the end of the paddle shaft in polyurethane blocks. The fan propellers were anchored to the frame above the water. It was also run at 100 rpm during treatment.

***Experimental design and process***

The experiment was carried out in six earthen ponds covered by canvas and includes 5 treatment methods and a control. As described in the section 2.2, the five mechanical treatment methods included for evaluation asplash board (SP), gutter (GT), diffused aerator system (DAS), paddlewheel (PD), porcupine-fan (PF) and a control (CT) treatment. Water volume was 1 $m^3$ with 1 $m^2$ surface area. Wastewater was collected during the third month of intensive (stocking density 200 − 250shrimps $m^{-2}$) shrimp farming cycle from the canal and then pumped into five treatment tanks and one control. The experiment was performed in six hours from 7:00 AM – 1:00 PM and replicated three times in June, 2011 at Dien Mon Enterprise Shrimp Farming, Truong Son Company, Thua Thien Hue province, Vietnam.

***Water quality variables and sampling***

The wastewater parameters monitored includedTemperature (T), pH, Salinity (S), Dissolved Oxygen (DO), Total Ammonia Nitrogen (TAN),and Ammonia ($NH_3$), measured with a different sampling frequency. In the first hour of treatment, the samples were measured every 20 minutes, then changed to every 30 minutes for the second hour and finally every 60 minutes for the last four hours of the treatment duration process.

Each sample was collected at five points in the tank including: 4 corners and the center at 30– 40 cm in depth (from the water surface) and then mixed together. One liter of wastewater was taken out from the homogenously mixed composite sample and stored in a PE bottle and then quickly analyzed using a test-kit. Samples were also preserved in cold conditions and immediately taken to the laboratory for analysis within 24 - 48 hours.

The concentration of DO, T, S and pH were measured using a water multi-parameters quality monitoring equipment probe (Model no.YSI 556MPS, YSI, USA) in the pondat three water depths (15 cm below water surface, 50 cm water column and 15 cm above tank bottom).

Total ammonia nitrogen was measured by the Phenate method (SMEWW-4500-$NH_3$-A) at the laboratory of Hue University of Agriculture and Forestry (HUAF), referred to(American Public Health Association (APHA), 2005)and the colorimetric methodwith a Sera water analysis test kit (Sera, 2000). The concentration of $NH_3$ toxicity was calculated based on the TAN, temperature and pH measurements. The concentrations of $NH_3$ during the experiment were calculated by using Eqs. 1 − 3:

$$K_a = \frac{[H^+][NH_3]}{[NH_4{}^+]} \quad (1)$$

where $K_a$ is the ammonia dissociation constant and calculated by Eq. 2 as referred to by Emerson et al.(1975):

$$pK_a = 0.09108 + \frac{2729.92}{273.2 + T} \quad (2)$$

where T is temperature in $^0C$.

Equation 2 was modified to Equation 3 to calculate the fraction of $NH_3$ in TAN concentration by Pano and Middlebrooks (1982).

$$\%NH_3 = \frac{100}{1 + 10^{(pK_a - pH)}} \quad (3)$$

Based on the three equations (1-3), online computation software was developed by SVL Analytical Inc, Environmental Analysis for the Mining Industry (SVL, 2010) used for calculated $NH_3$concentration.

***Statistical analysis***

The standard $O_2$ transfer rate (SOTR) of an aerating device is defined as the mass of $O_2$ that the device can introduce into a body of water per unit time at standard conditions (water temperature is $20^0$C, 0 $mgL^{-1}$ of initial DO concentration, one atmospheric pressure and clear tap water).

SOTR and aerator efficiency (AE) have been calculated by Eqs. 4 −7. They are based on the American Society of Civil Engineers (ASCE) standard method for aerator evaluations and have been investigated by Boyd and Tucker (1992).

$$SOTR = K_1 \times C_s \times V \quad (4)$$

Where STOR is standard oxygen transfer rate ($kgO_2h^{-1}$)

$K_1$ is the oxygen transfer coefficient at $20^0$C ($h^{-1}$)
$C_s$ is DO concentration at saturation at $20^0$C (mg $L^{-1}$)
V is tank volume ($m^3$)

$$K_1 = K_2 \times 1.024^{T-20} \quad (5)$$

where $K_2$ is the oxygen transfer coefficient at water temperature ($h^{-1}$)

T is water temperature during treatment ($^0$C)

The actual oxygen transfer rate for an aerator operating in a treatment pond can be estimated with the following equation:

$$\mathbf{OTR = SOTR \times \frac{C_s - C_p}{9.07} \times 1.024^{T-20} \times \alpha} \quad \textbf{(6)}$$

whereOTR is oxygen transfer rate ($kgO_2h^{-1}$)
$C_p$ is DO concentration in treatment pond water ($mgL^{-1}$)
T is water temperature ($^0$C)
is ratio value of oxygen transfer coefficient for test water and tap water

The DO enhancement efficiency ($kgO_2$ $kWh^{-1}$) was computed with the following equation:

$$\mathbf{AE = \frac{SOTR}{P}} \quad (7)$$

whereP is power of the motor (kW)

AE is aerator efficiency (kg $O_2kWh^{-1}$)

The following equation was used to calculate the oxygen transfer during treatment process:

$$\mathbf{= K_La(C_\infty - C_t)} \quad \textbf{(8)}$$

where$C_\infty$ is concentration in equilibrium with gas as given by Henry's law Saturated oxygen concentration in water (mg $L^{-1}$);
$C_t$ is concentration of oxygen in liquid bulk phase at time t, (mg $L^{-1}$)
C is concentration of oxygen in solution;
$K_La$ is the oxygen consumption coefficient (overall liquid film coefficient), ($h^{-1}$)
V is volume of water in treatment pond (L)

The oxygen transfer efficiency (OTE) of the equipment was calculated using Eq. 9:

$$\mathbf{OTE = \frac{OC}{A} \times 100} \quad (9)$$

Where OTE is the oxygen transfer efficiency of equment (%)
A is amount of oxygen supply at standard temperature pressure ($mgO_2$ $h^{-1}$)
OC is the total oxygen supply by equipment ($mgO_2$ $h^{-1}$)

Lloyd (1961) indicated that the theoretical value of toxicity can be calculated on consumption and that there is arelationship between DO concentration and the $NH_3$ toxicity removal and the estimate, is based on the slope of the linear equation. Myers et al.(2006) also suggested that the reduced oxygen supply and thus decreased DO concentration has resulted inan increased ammonia concentration.

Based on this principle and from the experimental data, linear regression analysis was used for investigating the correlation between DO enhancement and ammonia removal during the mechanical treatment operation. An estimate of the concentration of ammonia toxicity removal was given by the following relationship:

$$Y = ax + b \quad (10)$$

Where Y is the ammonia toxicity concentration
x is the DO concentration
a is slope of line
b is a constant

The removal of ammonia were calculated as

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (11)$$

Where R is the change of ammonia (%)
$C_0$ is the initial ammonia concentration (mg $L^{-1}$)
$C_t$ is the ammonia concentration at the end of treatment (mg $L^{-1}$)

All of the experiments were repeated three times. Data were subjected to analysis of variance (ANOVA) followed by Tukey's post hoc test at statistical significant levels ($p < 0.05$) using SPSS.

## Results

***Temperature, pH and salinity profile***

Mean values of pH, temperature and salinity offive different treatment methods and the control are showed in Table 1. The pH slightly decreased in all 5 treatments while it has increased in the control during the experiment period. The mean level of pH in treatment SP was low (7.52±0.18) while it was higher in the control (7.91±0.25) compared with other treatments. Statistical analysis indicated that there were significant differences in pHbetween the control and the five treatment methods. The results also indicated that pH in SP treatment was significantly different($p<0.05$) when compared with the other treatments except for GT treatment. Temperature in treatments was slightly lower than in the control while salinity was not different between treatments and the control.

***Enhancement of DO***

Fig. 2(a) showed that the concentration of DO increased during the experiment in all five treatment methods. While it increased in the first three hours of treatment in the control, later onthe trend for DO slightly dropped until the end of the treatment process. The DO concentration increased from 2.95±0.51 mg $L^{-1}$to >6 mg $L^{-1}$in all treatments while it increased only to 3.83± 0.61mg $L^{-1}$in the control after 6 hours of treatment. The concentration of DO increased to 6.64±0.42 mg $L^{-1}$ in the SP treatment and this was the highest level achieved when compared to other treatments. The order of DO level increase follows SP >GT > PF>PD >DAS> control.

Fig. 2(b) showed thatDO increase is higher in the first hour than in the following hours of the experiment in all treatments. In the first hour of the experiment, DO increased from 2.95±0.51 mg $L^{-1}$to 5.76±0.42 mg $L^{-1}$in treatment SP and followed in descending order of effectiveness as follows: GT (2.23±0.86 mg/L), PD (1.52±0.54 mg $L^{-1}$), PF (1.20±0.55 mg $L^{-1}$), DAS (0.95±0.44 mg $L^{-1}$) and control (0.79±0.45 mg $L^{-1}$). However, in the second hour, DO levels increased to the highest in the control (1.12±0.14 mg $L^{-1}$) but it quickly dropped in the third hour of treatment duration. DO in the five treatments increased until the end of the experiment and reached saturation. In the third hour of treatment, the concentration of DO in the control decreased to 0.49±0.22 mg $L^{-1}$and it continued to decrease until the end of the experiment. Comparing DO enhancement among the five treatment methods, the results indicated that SP treatment achieved higher levels than any other treatments.

The DO level in the SP treatment was raised up to 9.39±0.17 mg $L^{-1}$, while 6.13±0.35 − 7.61±0.28 mg $L^{-1}$was achieved by the other four treatments (GT, DAS, PD, PF) after 6 hours oftreatment. Moreover, the enhancement rate for DO in all treatments decreased with increasing treatment duration starting from the third hour of the experiment but it was higher than that in the control during the 6 hours of experiment. Linear regression equation analysis was applied to compare DO enhancement levels with time by the five mechanical treatment methods and the control and results are shown in Table

2. Theresults indicated that DO and time of treatment process weresignificantly related. The correlation coefficient ($R^2$) in all the treatments were higher than 0.84. The $R^2$ value in SP treatment was 0.96 while it was only 0.41 in the control. These results suggest that DO in treatment ponds mostly depend on the oxygen supplied by the treatment equipment. The DO fluctuates in the control pond due to several factors such as temperature, salinity, pH, toxic gases level, biodegradation processes and also the growth rate of algae.

***Removal of TAN***

Fig. 3(a)indicated that, the concentration of TAN was reduced from 4.96±0.56 mg $L^{-1}$to 0.27±0.02 mg $L^{-1}$in SP treatment (95%) in 6 hours. TAN concentrations for other treatments were also reduced during the experiment, but the removal rate was lower than that in SP treatment. TAN reduced from 4.96±0.56 mg $L^{-1}$to 1.80±0.22 mg $L^{-1}$, 2.09±0.15 mg $L^{-1}$, 2.33±0.26 mg $L^{-1}$, and 2.09±0.15 mg $L^{-1}$in treatments GT, DAS, PD and PF, respectively. The reduction of TAN concentration in the control was lowest and the level by the end of treatment was still 3.86±0.04 mg $L^{-1}$. After 4 hours of treatment, TAN levels increasedin the control while in five treatment tanks, TAN decreased with increasing treatment duration. In treatment tanks, $O_2$was diffused in to the water facilitatedby mechanical equipments. The nitrification process occurs readily and most of the $NH_3$ has been converted to other nitrogen forms (nitrite and nitrate). In the control, the concentration of DO decreased with increasing treatment duration resulting in increasing TAN concentration.

In the first hour of the experiment, the removal rate of TAN achieved was higher than that in the subsequent experimental hours. In treatment SP, the amount of TAN removed was up to 1.82, 1.12 and 0.94 mg $L^{-1}$in the first, second and third hour of the experiment, respectively(Fig. 3b). Comparing the five treatment methods for TAN treatment efficiency, results indicated that SP treatment achieved higher TAN removal than that in any other treatments or the control. The SP treatment achieved maximum TAN removal efficiency at 94.6±3.4% while the minimum TAN removal efficiency in DAS treatment was only 40.4±4.5%. However, all five treatment methods achieved higher TAN removal efficiency than that in the control and were significantly different ($p<0.05$). In the control tank, TAN concentration reduced only by 19.3±4.9% in the six hour process. The wastewater used in this experiment was at the third month of the shrimp production crop when nutrient pollutants are inrelatively higher concentrates in the wastewater. On the other hand, the treatment efficiency depends on the initial level of$NH_3$, so if the initial $NH_3$concentration is higher, the treatment duration is also increased. This suggests that SP treatment was able to remove TAN from effluent to meet the aquaculture standard (TAN ≤ 2 mg $L^{-1}$) within an hour of treatment commencing.

***Removal of $NH_3$ toxicity***

The concentration of $NH_3$ in all treatments was calculated based on the TAN concentration and the average of pH and temperature values, according to Equations 1-3. The removal of $NH_3$ by aerator equipment is presented in Fig. 4(a) and Table 3. The $NH_3$ levels decreased in all treatments but increased in the control after one hour of treatment. Fig. 4 (b)indicated that $NH_3$ in the control slightly decreased from 0.19 mg $L^{-1}$to 0.18 mg $L^{-1}$in the first hour but significantly increased from 0.18 mg $L^{-1}$ to 0.26 mg$L^{-1}$and 0.4mg$L^{-1}$in the second and third hours of the experiment, respectively. While in all treatments $NH_3$ decreased quickly in the first two hours and treatment SP was observed to have the highest reduction. The $NH_3$ was reduced more than 78% (approximately 0.15 mg $L^{-1}$) within two hours and up to 99.3±1.28% with 6 hours of treatment using SP treatment followed in order by: GT (76.8±2.41%) > PF (63.6±13.9%)>PD (55±11.9%) >DAS (44.4±20.03%) while in the control, $NH_3$ increased from 0.19±0.07 mg $L^{-1}$to 0.52±0.32 mg $L^{-1}$ (0.33±0.27 mg$L^{-1}$). Statistical analysis indicated that $NH_3$ removal was significantly different between the 5 treatments and the control and between treatment SP and the 4 other treatments (DT, PD, PF and DAS) with $p<0.05$ but no significant differences were found among the four treatments GT, PD, PF and DAS ($p>0.05$).

***Oxygen transfer and aeration efficiency by five mechanical treatment methods***

The mean temperature during the experiment was $30^0$C, and the volume of the tank was 1000 L. Based on Eqs.4 − 9, the OTR, AE and OTE of the fivemechanical treatment methods have been calculated and the results are presented in Table 5. The highest and lowest of OTR, AE and OTEvalues were achieved in treatment SP and the treatment DAS, respectively.

***Relationship between oxygen diffuser and removal of $NH_3$toxicity when using the mechanical treatments***

Linear regression analysis was used to investigate the relationship between DO enhancement and removal of ammonia toxicity when using mechanical equipments to treat intensive shrimp farms effluent. The statistical analysis indicated that the removal rate of $NH_3$ toxicity is dependent on the amount of oxygen facilitated by equipment with the correlation coefficient ($R^2$) of 0.603 ($p<0.05$). The statistical analysis also indicated that the $NH_3$toxicity concentration is decreased by 0.033 mg $L^{-1}$ per unit increase in DO level (1 mg$L^{-1}$) during the treatment (Fig.5).

## Discussion

The pH, temperature and salinity are important chemical parameters that need to be considered because they have a significant effect on the metabolism and other physiological processes in shrimp culture. Moreover, the percentage of $NH_3$ toxicity in TAN is dependent on pH and temperature values. The $NH_3$ toxicity level increases with increasing pH and temperature but decreases with increasing DO concentration during treatment. The same was further reported in several researches such as Bower and Bidwell (1978), Cheng et al. (2003), Hopkins et al. (2007) and Jensen and Andersen (1992). However, the informationon pH, temperatureandsalinitychanges is limited during oxygen diffusion facilitated by mechanical treatment.This study investigated the change of pH, temperature and salinity using five different mechanical equipments for the enhancement of DO and removal of $NH_3$ toxicity. Salinity was not significantlychanged in treatments and control. The minor changes of salinity only depended on initial values of wastewater quality while temperature and pH decreased slightly in all five treatments and increased in the control during the experimental period. The level of pH in SP treatment was lower compared with the other treatments, except for GT treatment. The pH and temperature in the treatments were usually lower than in the control. Because, in treatment tanks when the oxygen is diffused into the tanks, the biodegradation of organic matter will occur to a greater extent than that in the control tank, and the result of this processis reduced pH and temperature. While algal bloom is greater under anaerobic conditionsin the control tank resulting in slightly increased pH and temperature levels, the changes of pH and temperature wasnot only dependent on oxygen diffusionperformance of mechanical equipment but also on many factors such as phytoplankton and zooplankton density, and biological processes(Buentello et at., 2000). On the other hand, the DO level depends on the concentration of dissolved carbon dioxide ($CO_2$) present in pond water without aeration or pH control(Summerfelt et al., 2001).

At the beginning of the treatment duration, oxygen wasdiffusedfrom atmospheric air by the facilitation of equipment and readily enters the water surface resulting inquickly increased DO concentration to reach saturation in the water surface. The amount of oxygen that diffused from the surface throughout the entire water column was slower than the initial entry of oxygen into the surface layer. Thus, the water surface quickly saturated with DO, and the oxygen diffusion rate into deeper water layers becomes slower. Although, oxygen was still facilitated by the equipment, it cannot diffuse from atmospheric air into the surface film until some of this oxygen has diffused into the water column. Therefore, the mechanical devices must be tested for their ability to not only mix air with the upper water layer but also to mix the oxygen-enrichedupper water layer with the oxygen-poor lower water layer to increase the total oxygen content of the water. The optimization of experimental duration to maximize the DO enhancement requires not only a shorter treatment duration to reduce energy consumption for equipment operation but also increased amount of water recyclingto improve treatment efficiency. The results of this study suggest that two mechanical treatment methods (splash board and gutter)had achieved a higher DO level in shrimp wastewater than the minimum required level (4 $mgL^{-1}$) for fish and mangrove snail culture within an hour of treatment.

In general, there are three basic ways for enhancing $O_2$ transfer into water: gravity aerators, mechanical aerators, and pure oxygen contact systems. Pure oxygen systems have limited use in aquaculture ponds while mechanical aerators such as paddlewheels, diffuser aerator systems and propeller-aspirator-pumps are commonly used to aid in the distribution of DO throughout ponds (Boyd, 1998). A wide variation in performance of aeration in term of AEwas found: 1.17 $kgO_2kWh^{-1}$(Taiwanese paddlewheel), 1.03 $kgO_2kWh^{-1}$(Japanese paddlewheel), 0.85 $kgO_2$ $kWh^{-1}$(Thai paddlewheel), 2.25 $kgO_2kWh^{-1}$(Auburn University design), 1.656 $kgO_2$ $kWh^{-1}$(Indian paddlewheel) and 3.79 $kgO_2kW^{-1}h^{-1}$(Brazilian paddlewheel) (Boyd, 1998; Moulick et al., 2005; Ruttanagosrigit et al., 1991; Vinatea and Carvalho, 2007). The results of the present study showed that a maximum AE of only 0.504 $kgO_2$ $kWh^{-1}$and 0.575 $kgO_2$ $kWh^{-1}$are achievable with paddlewheels and porcupine-fans, respectivelyused in Vietnam. This suggests that the design of the particular paddlewheel and porcupine-fans used for the study need to be modified and optimized to achieve higher efficiency. For propeller-aspirator-pump aerators, several studies have been conducted to test the standard oxygen transfer rate and these results showed that the aeration efficiencieswere 3.62 $kgO_2kWh^{-1}$(made in Brazil) (Vinatea and Carvalho, 2007), 1.25 $kgO_2kWh^{-1}$(made in the USA) (Ruttanagosrigit et al., 1991) and 0.42 $kgO_2kWh^{-1}$ (made in Taiwan) (Moulick et al., 2005). Other equipments have been developed for supplying oxygen in wastewater such as ozone and air injection systems under high pressure and the aeration efficiency of these system were 1.18 $kgO_2kWh^{-1}$ and 1.41 $kgO_2kWh^{-1}$, respectively (Mongkol and Suntud, 2008). However in the present study, the aeration efficiency of the diffuser aerator system was only 0.89 $kgO_2kWh^{-1}$. It was higher than propeller-aspirator-pump aerators made in Taiwan but lower than other propeller-aspirator-pump aerators from other countries.

In this study, equipment devices were running in shrimp wastewater with relatively high levels of pollutants, but these were not only investigated for increasing DO levels but also for removing toxic $NH_3$ gas. While most aerator equipment used for supplying $O_2$ into the aquaculture ponds have been reviewed, information was lacking about the gas exchanges process.This research also presented the aeration efficiency of other equipments such as splash boards and gutters. The results indicate that the aeration efficiencyvalues of treatment SP and GT at the optimized conditions were 2.21$kgO_2kWh^{-1}$ and 1.55 $kgO_2kWh^{-1}$, respectively. These results were similar to the aerator efficiency of paddlewheels and propeller-aspirator-pump aerators used in previous research. Recently research recommends that structural parameters such as hole density and slope can be adjusted to provide an optimum condition for maximizing the performance of the splash board and gutter(Nguyen, 2013). The literature review suggested that the treatment performance of commonly used equipments such as paddlewheel, diffuser aerator systems and propeller-aspirator-pump not only depended on many factors such as structural, material use, power supply, energy consumption, company brand specifications but also depend on salinity, and temperature (Fast et al., 1999; Kumar et al., 2010). These equipmentsmay also be optimized for improving their treatment performance in accordance with specific requirements and local conditions.

Boyd (1998), Pillay and Kutty(2005) and Jiang et al.(2004) reported that ammoniacal N exists in two forms: un-ionized ammonia ($NH_3$), and ionized ammonium ion ($NH_4^+$) and the percentage of $NH_3$ depends on water pH and temperature values. Sommer and Olesen (1991) found temperature and pH to be the two most important factors that influence $NH_3$ volatilization. In general, pH in pond is at a low level in the morning and increases in the afternoon which results in increasing toxic $NH_3$ concentration in the afternoon. However, in this study when using mechanical treatments to enhance DO and remove ammonia toxicity, the fluctuation of $NH_3$ is not following the pH trend because $NH_3$ concentration depends on a number of other factors. One of the most important factors is the DO concentration in the water(Wajsbrot et al., 1990)which influences the $NH_3$levels. The concentration of DO increased in all treatments but at different rate during the application of the five mechanical devices. Since, the amount of $NH_3$ reduction strongly depends on $O_2$ supply level, which in turn affectedpH. The present study indicates that SP treatment achieved the highest DO concentration and greatest reduction of $NH_3$ which may suggest that the removal rate of $NH_3$ increased when increasing the DO supplied in the treatment of shrimp wastewater by mechanical treatment.

In the last decade, many methods have been developed to remove TAN including both physiochemical treatments (ion exchange, reverse osmosis, electrodialysis or activated carbon adsorption) and biological treatments (trickling filters, fluidized bed reactor, rotating biological contactor, biofloc technology and wetlands) (Mook et al., 2012). Most of these methods showed a significant benefit in the removal of TAN. The physicochemical methods achieved the removal of TAN of around 75.42% − 85.30% (ultra-low pressure polyethersulfone membrane) 90 − 97% nitrogen removal (wind drive reverse) and 89.36% nitrogen removal (Ion exchange membrane bioreactor) (Mook et al., 2012). However, membrane and ion exchange methods are usually expensive and also difficult to operate. It is not potential to apply these methods to shrimp production in developing countries. Biological methods also showed that they could achieve higher efficiency for treatment of TAN and removal of other nitrogen sources. Trickling filters achieved removal of up to 65.21% of TAN, the rotating biological contactor can remove 40% of TAN and biofloc technology can remove around 80.49 − 95% of-TAN(Mook et al., 2012). But these methods have not only high risk of clogging but also higher cost of operation. Other biological treatments such as wetlands have the potential to remove nitrate and suspended solids. Naylor et al. (2003) has reported 44.1%−69.7% of $NO_3$removal by six subsurface wetlands. However, the wetland method not only requires longer treatment time but also needs greater land areas for reaction than other methods. The present study investigated the ability of five different aerator mechanical equipments to remove $NH_3$ toxicity gas based on enhancing oxygen levels. The experimental results show that mechanical equipments not only enhance DO but can also remove $NH_3$toxicity from shrimp wastewater. They are able to reduce 40.4 − 94.6% of TAN and up to 99.3% of $NH_3$ within six hours of treatment. Although, the treatment efficiency of the aerator devices presented in this research is lower than that of other methods such as ion exchange membrane bioreactors or the trickling filter method. In addition, the removal of $NH_3$ toxicity from shrimp wastewater also depends on other factor such as pH level, temperature, $CO_2$ and theefficiency of nitrification process in treatment tank whereas the nitrification rate is controlled bybacterial species and densities. However, mechanical treatment equipment such as splash board and gutter are simple and user friendly in operation. They also have low cost in operation, require less energy and are short in treatment duration process compared with other treatment methods.

## Conclusions

This study was conducted with five mechanical devices (splash board, gutter, diffuser aerator system, paddlewheel and porcupine-fan) to diffuseair into wastewater.All these five treatment devices tested are potential not only to enhancement ofDO but also to remove toxic $NH_3$ gas from shrimp farming wastewater. The treatment efficiency was significantly different among the five treatment methods in whichthe SP method achieved the highest treatment performance, and was found to be the most advantageous for the diffusion of $O_2$and removal of $NH_3$ toxicity from shrimp effluent. It needed only three hours for the enhancement of DO levelto $\geq$ 4 mg $L^{-1}$ and removal of $NH_3$toxic gases to $\leq$ 0.01 mg $NH_3L^{-1}$ in order to meet the required aquaculture wastewater standard for discharge into the environment.

Splash board also showed thelowest energy consumptioncompared with four other treatment methods. The aeration efficiency and $O_2$transfer efficiency of the splash board were 2.21 $kgO_2kWh^{-1}$ and 15.56% while these were lower than 1.5 $kgO_2kWh^{-1}$ and 11% in the other four treatment methods.

Although, splash board treatment showed greater benefit and applicability for treatment of wastewater from intensive shrimp farming, it should still be modified to achieve higher performance. In addition, other equipments that include paddlewheel, diffuser aerator systems and porcupine-fanmay be optimized for improving the treatment performance.

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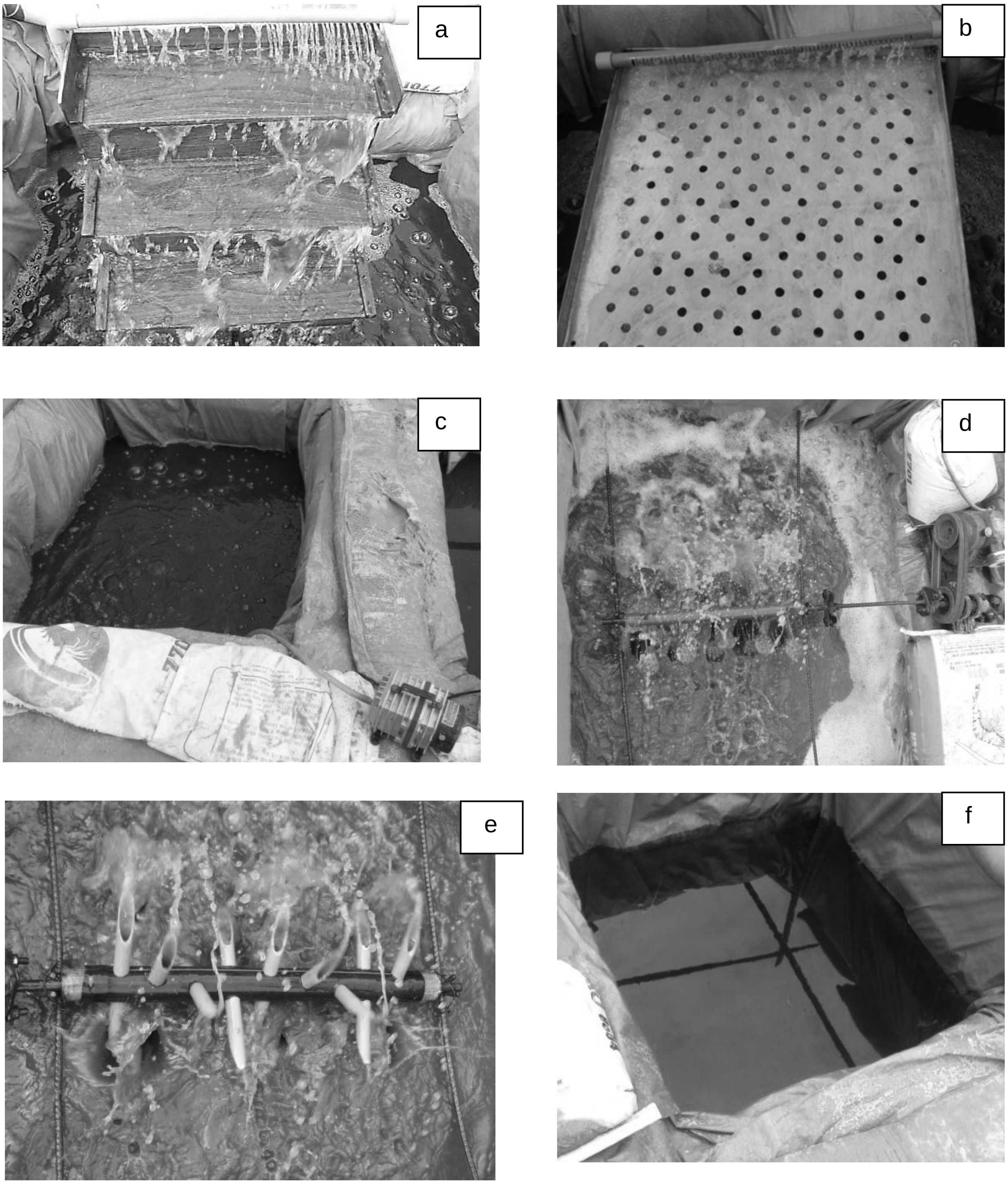
**Fig. 5**. Correlation of $NH_3$ toxicity removal and DO enhancement in all treatment by five mechanical methods

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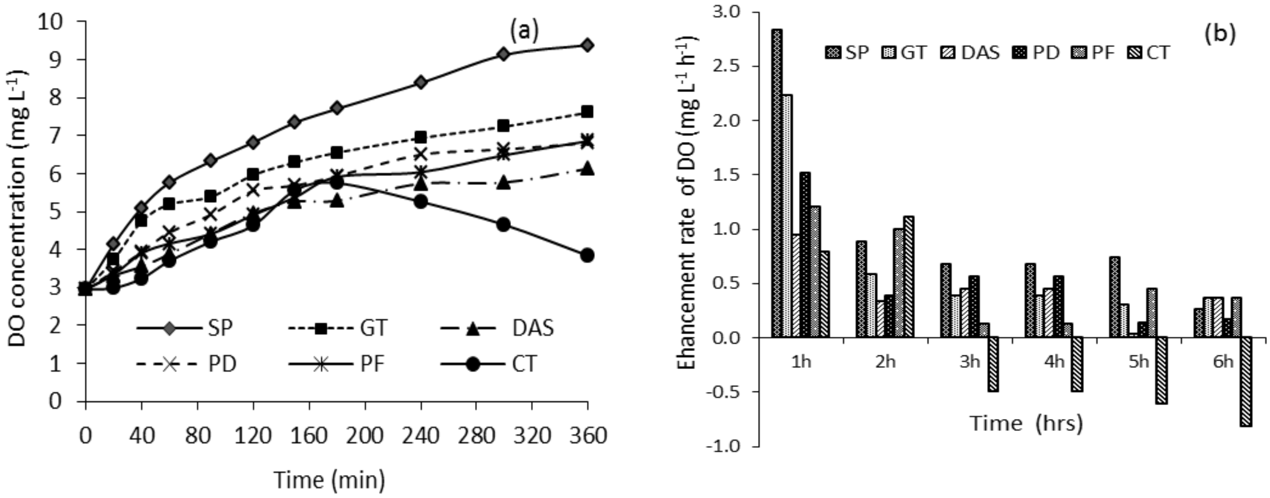


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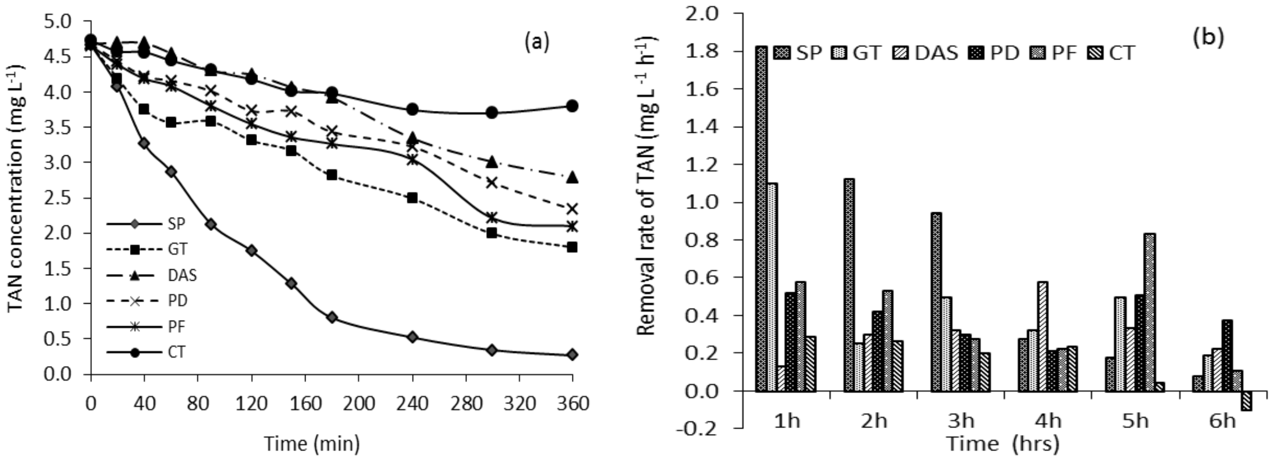


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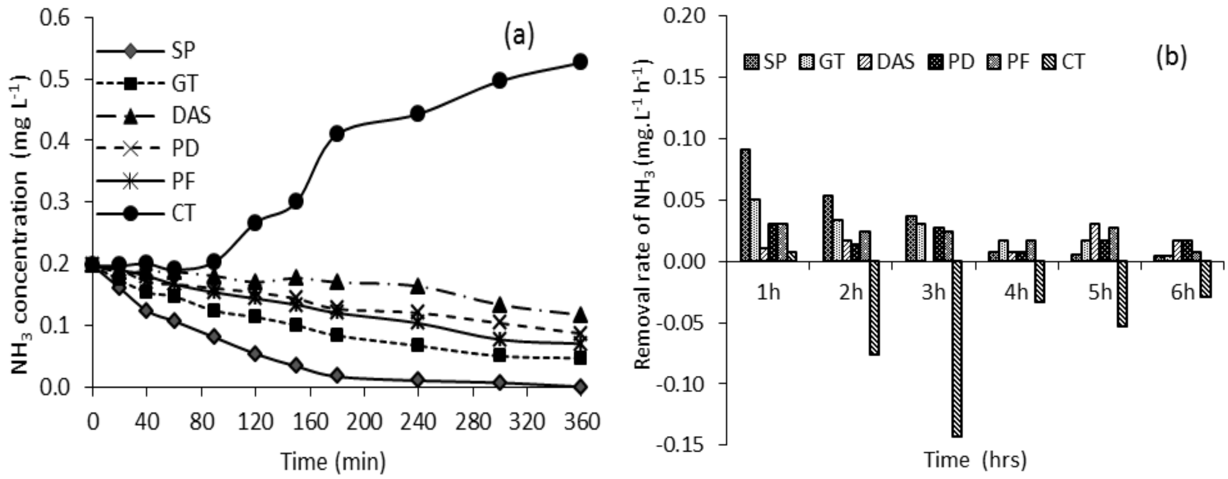


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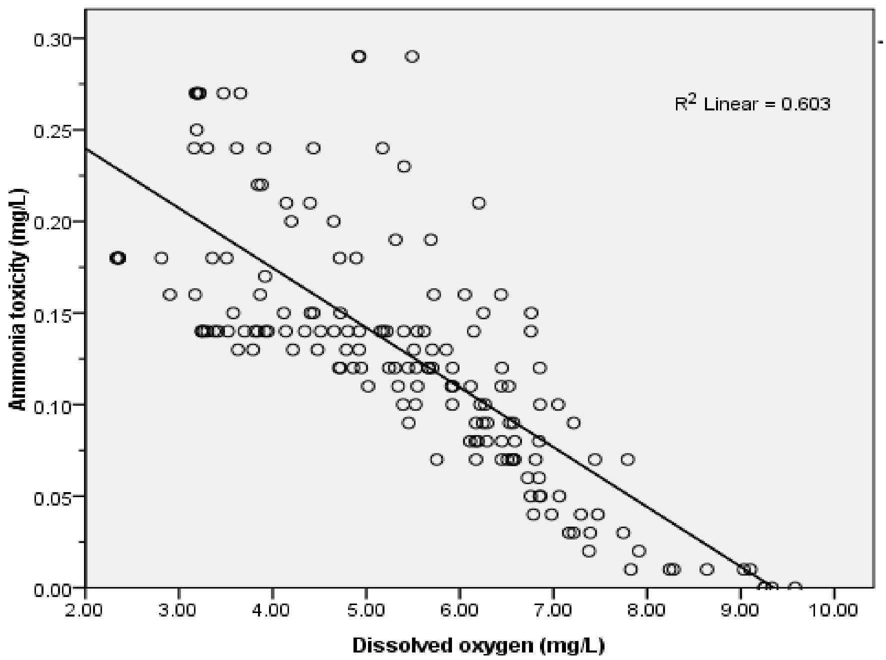


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**Table 5** Specific Parameters Of Five Mechanical Treatment Methods

**Table 1**

Mean (±SD) of pH, temperature (T) and salinity (S) values in five treatments and a control during the experiment

| Parameters | Treatments | | | | | |
|---|---|---|---|---|---|---|
| | SP | GT | DAS | PD | PF | CT |
| pH (log $H^+$) | 7.52±0.18[a] | 7.58±0.15[ab] | 7.68±0.15[b] | 7.65±0.10[b] | 7.76±0.12[b] | 7.92±0.25[c] |
| T ($^0$C) | 30.23±0.68[a] | 30.3±0.83[a] | 30.76±0.28[b] | 30.34±0.91[a] | 30.47±0.59[a] | 31.14±0.45[b] |
| S (‰) | 17.98±0.49[a] | 17.97±0.62[a] | 17.71±0.56[a] | 17.05±0.64[a] | 17.94±0.67[a] | 17.90±0.64[a] |

Values are mean ± standard deviation; n=3 for all treatments
[a,b, c] One way ANOVA mean the same row follow by different letters indicate significantly different by the Tukey's test ($p<0.05$)
SP: Splash board; GT: Gutter; DAS: Diffuser aerator system; PD: Paddlewheel; PF: Porcupine-fan; CT: Control

**Table 2**
Mean (±SD) initial, final concentration, the enhance level and regression equation of dissolved oxygen (DO) in five treatments and a control

| Treatments | Initial (mg $L^{-1}$) | Final (mg $L^{-1}$) | Enhancement (mg $L^{-1}$) | Regression equation | $R^2$ |
|---|---|---|---|---|---|
| SP | 2.95±0.51 | 9.39±0.17 | 6.64±0.42[a] | y=0.61x + 2.978 | 0.96 |
| GT | 2.95±0.51 | 7.61±0.28 | 4.65±0.25[b] | y=0.43x + 3.100 | 0.92 |
| DAS | 2.95±0.51 | 6.13±0.35 | 3.20±0.19[c] | y=0.33x + 2.708 | 0.84 |
| PD | 2.95±0.51 | 6.81±0.07 | 3.78±0.43[c] | y=0.38x + 2.778 | 0.94 |
| PF | 2.95±0.51 | 6.87±0.27 | 3.91±0.67[bc] | y=0.39x + 2.593 | 0.85 |
| CT | 2.95±0.51 | 3.83±0.61 | 0.93±0.34[d] | y=0.21x + 3.000 | 0.41 |

Values are mean ± standard deviation; n=3 for all treatments
[a,b, c,d] One way ANOVA, mean the same column follow by different letters indicate significant different by the Tukey's test ($p<0.05$)
SP: Splash board; GT: Gutter; DAS: Diffuser aerator system; PD: Paddlewheel; PF: Porcupine-fan; CT: Control

**Table 3**
Mean (±SD) initial, final concentration, the removal level and regression equation of total ammonia nitrogen (TAN) in five treatments and a control

| Treatments | Initial ($mg\ L^{-1}$) | Final ($mg\ L^{-1}$) | Reductions ($mg\ L^{-1}$) | Reductions % | Regression equation | $R^2$ |
|---|---|---|---|---|---|---|
| SP | 4.96±0.56 | 0.27±0.02 | 4.39±0.34[a] | 94.61±3.400 | y= -0.457x + 4.739 | 0.92 |
| GT | 4.96±0.56 | 1.80±0.22 | 2.87±0.41[b] | 61.35±2.98 | y= -0.262x + 4.782 | 0.87 |
| DAS | 4.96±0.56 | 2.79±0.43 | 1.89±0.28[bc] | 40.42±4.49 | y= -0.197x + 5.211 | 0.73 |
| PD | 4.96±0.56 | 2.33±0.26 | 2.34±0.37[b] | 50.01±4.55 | y= -0.212x + 4.968 | 0.84 |
| PF | 4.96±0.56 | 2.09±0.15 | 2.55±0.56[b] | 54.48±6.42 | y= -0.246x + 4.985 | 0.85 |
| CT | 4.96±0.56 | 3.86±0.40 | 0.93±0.35[c] | 19.30±4.91 | y= -0.107x + 4.829 | 0.48 |

Values are mean ± standard deviation; n=3 for all treatments
[a,b, c] One way ANOVA, mean the same column follow by different letters indicate significant different by the Tukey's test ($p<0.05$)
Minus is mean the value at the end is higher than that in the initial values of the experiment
SP: Splash board; GT: Gutter; DAS: Diffuser-air aerator system; PD: Paddlewheel; PF: Porcupine-fan; CT: Control

**Table 4**
Mean (±SD) initial, final concentration, the removal level and regression equation of ammonia ($NH_3$) toxicity in five treatments and a control

| Treatments | Initial ( $mg\ L^{-1}$) | Final ( $mg\ L^{-1}$) | Reduction $mg\ L^{-1}$ | Reduction % | Regression equation | $R^2$ |
|---|---|---|---|---|---|---|
| SP | 0.19±0.07 | 0.001±0.0 | 0.189±0.06[a] | 99.26±1.28 | y= -0.020x + 0.19 | 0.84 |
| GT | 0.19±0.07 | 0.05±0.02 | 0.15±0.051[a] | 76.81±2.41 | y= -0.015x + 0.20 | 0.72 |
| DAS | 0.19±0.07 | 0.12±0.08 | 0.08±0.031[b] | 44.4±20.03 | y= -0.007x + 0.21 | 0.10 |
| PD | 0.19±0.07 | 0.08±0.03 | 0.11±0.046[a] | 55.03±11.9 | y= -0.001x + 0.21 | 0.46 |
| PF | 0.19±0.07 | 0.07±0.05 | 0.13±0.051[a] | 63.58±13.9 | y= -0.013x + 0.22 | 0.59 |
| CT | 0.19±0.07 | 0.52±0.32 | -0.330±0.27[c] | -157.67±88 | y= 0.037x + 0.09 | 0.39 |

Values are mean ± standard deviation; n=3 for all treatments
[a,b, c] One way ANOVA, mean the same column follow by different letters indicate significant different by the Tukey's test ($p<0.05$)
Minus is mean the value at the end is higher than that in the initial values of the experiment
SP: Splash board; GT: Gutter; DAS: Diffuser aerator system; PD: Paddlewheel; PF: Porcupine-fan; CT: Control

**Table 5**
Specific parameters of five mechanical treatment methods

| Parameters | Unit | Treatments SP | GT | DAS | PD | PF |
|---|---|---|---|---|---|---|
| $K_La$ | $h^{-1}$ | 2.27 | 1.59 | 1.11 | 1.46 | 1.48 |
| OTR | $kgO_2\,h^{-1}$ | 20.59 | 14.42 | 10.06 | 13.24 | 13.42 |
| AE | $kgO_2\,kWh^{-1}$ | 2.213 | 1.55 | 0.89 | 0.504 | 0.575 |
| OTE | % | 15.16 | 10.62 | 7.41 | 9.75 | 9.88 |

$K_La$: oxygen consumption coefficient; OTR: oxygen transfer rate; AE: Aerator efficiency; OTE: oxygen transfer efficiency