

An Ammonia Removal for Red Craw Crayfish Nursery Water Pond by using Electrocoagulation Method

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Abstract: This paper propose the method of ammonia removal of red craw crayfish nursery water pond. The ammonia in water pond has caused from red craw crayfish waste which effect to baby red craw crayfish to have strain, anorexia, slow growth and may die. Normally, the ammonia in aquaculture water has been founded in form of unionized form (NH_3) and ionized form (NH_4^+) which can measured by electrode sensor and transform in ammonia intensity (mg/L). The nursery pond system should be control ammonia in water less than 0.01 mg/L for safety and high growth condition. In this paper, the electrocoagulation method which based on electrochemistry principle is presented for ammonia removal. The two of aluminum electrodes are used to be an anode and cathode which receive direct current positive and negative to electrode respectively. An oxidation-reduction (redox) reaction has impact to aluminum ion separation, flocculation, floatation and sedimentation with ammonia particle. The input parameter of this reaction such as types of electrodes, area of electrodes (cm^2), voltage level (V), magnitude of current (A) and current density (A/cm^2) are studied. The output parameters of reaction such as TDS (Total Dissolved Solid), EC (Electrical Conductivity), pH and ammonia intensity are focused. The economic aspect is concerned in term of energy cost and corrosion of aluminum material quantity. The result found that electrocoagulation method can remove ammonia intensity from from 1.8 mg/L to 0.8 in 30 minutes and 0.8 mg/L to 0.05 mg/L in 30 minutes for 10 liters reactor chamber by using energy consumption 3.75 kWh/ m^3 or 15 bath/ m^3 .

Keywords: electrocoagulation, ammonia removal, red craw crayfish

1. Introduction

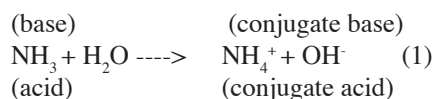
A red craw crayfish is one of the essential freshwater aquatic animal in northern which use for beautiful and also delivery as shrimp meat to food shop, restaurant and hotel. Because of easy breeding and shrimp embryo has no complex development and variety eatable food. The red craw crayfish take 4 months for growth period and well-grow in Thailand terrain and climate. However, the important factor such ammonia content should be controlled for less than 0.01 mg/L especially within one month of nursery pond of baby red craw crayfish. In case of high amount of ammonia content, baby red craw fish has strain, anorexia, slow growth and dead in 24-72 hours. Therefore the ammonia removal is essential process of nursery red crawfish in many method such as biological and chemical. However the above method still has drawback follow as need high area, time consume, low efficiency and high cost of chemical adding and energy consumption. In this research, the novel method which has high efficiency, small area, less time of reaction and no chemical adding such electrocoagulation is proposed.

2. Theory

2.1 Ammonia in Aquaculture

Nitrate and ammonia are the most common forms of nitrogen in aquatic systems. Ammonia is excreted by animals and produced during decomposition of plants and animals, thus returning nitrogen to the aquatic system. The ammonia has occur from nitrogen cycle which locate in the 2 forms follow as ionized ammonia, NH_4^+ and un-ionized ammonia NH_3 (Randall, 2002; Wajsbroet et al; Gupta et al, 2015; Capodaglio1) The unionized form (NH_3) is highly toxic to organism, other aquatic and human life than NH_4^+ 50 times. Ammonia can be toxic, causing lower reproduction and growth, or death as shown in Table1. Ammonia is a nutrient that contains nitrogen and hydrogen. The amount of ammonia is composed of total ammonia (mg/l), un-ionized ammonia (mg/l), total ammonia (as N, mg/l), un-ionized ammonia (as N, mg/l). Ammonia in water is equilibrium between unionized ammonia or free ammonia, NH_3) and NH_4^+ in the ionized form is written in equation (1). (Rogers, 1985).

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**Table 1** Free ammonia level and effect to red craw crayfish

Free ammonia NH ₃ (mg/L)	Effect to red craw crayfish
< 0.1	Safety
0.1-0.4	slow growth rate
> 0.4	strain, anorexia, die

The Factor effect to toxic of ammonia

The various factor has effects to toxic ammonia follow as DO, pH, variation of ammonia, exercise and resting animal and stress of animal and temperature.

Dissolved oxygen

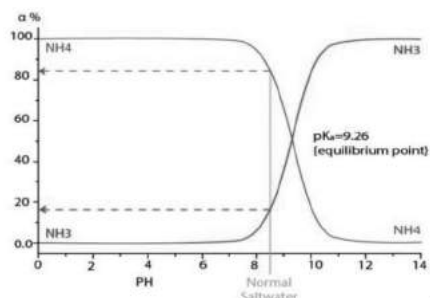
The ammonia toxic has increase when DO is decrease pass saturation point seabream (Silapchai and Srikanth, 2009). The appropriate Dissolved oxygen is around than 3-6 mg/L. Thus DO pump is also used to generate DO in water as shown in Fig.1 and Table 2.

Table 2 size of DO pump

Size of pond (litre)	500	1000	2000	3000	4000	5000	6000
Pump size (litre/min)	5	10	20	30	40	50	60

**Fig.2** DO pump

b) pH of water has effect to toxic of ammonia when pH increase, unionized ammonia has increase and more toxic. Chemical equilibrium ammonia is controlled by pH which NH_3 and NH_4^+ are transformed between each other upon the pH. The neutral acid-alkaline conditions should be about 7.0-8.0. When pH increase more than 7.5 NH_4^+ has decrease where as NH_3 has increase as shown in Fig. 3

**Fig.2** effect of pH to ammonia transform**c) Variation of ammonia level**

The aquatic animal has tolerance to constant ammonia level than variation of ammonia level which increase every hour from excretion

d) Exercise

The exercise aquatic animal has high ammonia than resting animal which ammonia level occur from decomposition of adenylate to inosinemonophosphate (IMP) and ammonia ion NH_4^+ .

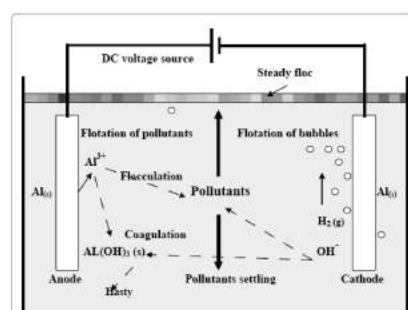
e) Stress condition

The ammonia will be increased when animal has stress from environmental condition such as congestion of animal, interval and size of animal, feeding and acclimation.

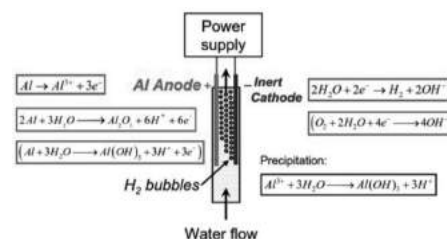
f) The temperature is an important factor of red craw fish treatment which should be controlled at 20-29 celsius by ventilation fan or heat lamp. If temperature high or low, the red craw fish may Anorexia, dodge in the shelter and rust stains at the claws.

2.2 Principle of electrocoagulation

The principle of electrocoagulation composed of DC power supply source, two electrodes for anode and cathode, which oxidation reaction is occur at anode and reduction reaction of water at cathode. By water are separated to generate H_2 and OH^- . After reaction for a while the water is transform to base and the sediment of aluminum ion which sediment color, particle in the water. The bubble gas is attached to sediment and float to surface which call "electro-floatation". (Drouiche et al, 2009; Kim et al., 2016; Holt et al, 2004; Babu et al, 2007)

**Fig.4** Principle of electrocoagulation

The reaction equations of electrocoagulation are composed of redox and oxidation reaction. Both anode and cathode electrode are aluminum and reaction in each electrode is shown in Fig. 2. The low density particle is float on the surface and the heavy particle is sediment in to the bottom.

**Fig.4** Redox–Oxidation of electrocoagulation

Effect of Electrocoagulation [12-16] (Kuokkanen et al, 2013; Zodi et al, 2009; Heffron and Mayer, 2016; Nepo et al., 2017; Bazrafshan et al, 2006).

a) Type of electrode : In most studies reported in the literature, aluminium (Al), iron (Fe), mild steel and stainless steel (SS) electrodes have been used as electrode materials. The aluminum is one of the attractive electrodes which has appropriate characteristic for electrocoagulation. A plenty of aluminum is found as the third rank of metal at earth crust, it has white color, light weight, hard, no brittle and easily transform in any form. The aluminum can make fast response reaction with other metal and give oxidation number +3. When Al^{3+} is in the water, it has capability to occur hydration reaction and hydrolysis. In this experimental, two electrode of aluminum is designed for anode and cathode of electrocoagulation reactor. The size of the cation produced ($10\text{-}30\mu\text{m}$ for Fe^{3+} compared to $0.05\text{-}1\mu\text{m}$ for Al^{3+}) was suggested to contribute to the higher efficiency of iron electrodes. (K. Jo Kim et al., 2016).

b) Current Density : The most critical operation parameters in electrocoagulation which have integral effect on process efficiency is current density. The current density is calculated the ratio of Current and Area of Electrode as shown in equation (2)

$$J = I/A \quad (2)$$

where A is cross section area and I is current (A) and when the potential voltage occur between electrode then current density and electric field are generated as shown in equation (3)

$$J = \sigma E \quad (3)$$

Where σ is electrical conductivity and E is electromotive force

c) Effect of water conductivity and supporting electrolyte (σ) : The high water conductivity has increase the efficiency of electrocoagulation. Sodium chloride is usually employed to increase the conductivity of the water or wastewater to be treated

d) Effect of pH : The value display the positive potential of the hydrogen ions (pH) is express the concentration of H^+ or Hydronium ion (H_3O^+) which use for indicate acid or base of solution. The pH of the reaction solution changes during the EC process, and the final pH of the effluent actually affect the overall treatment performance. It is generally found that the aluminium current efficiencies are higher at either acidic or alkaline conditions than at neutral.

e) Inter-electrode spacing and configuration : The space between electrode will increase treatment efficiency but it increase the capital cost of material. The electrode configuration connection is up to requirement of treatment method. If the system want to remove the suspend solid by float particle, the electrode should line in vertical in order to make a gas bubble from chemical reaction take the particle with float sediment. If the system want to remove suspend solid with sedimentation, the electrode should be layout in horizontal which anode is line below and cathode is line upper.

f) Electrolysis time: Increasing of electrolysis time leads to an increase in coagulant concentrations that has been reported to reduce the floc density, then to reduce their settling velocity (Zodi et al., 2009).

g) Efficiency : The dissolution of the anode metal is based on Faraday's law as shown in equation (4)

$$m_{\text{metal}} = \frac{ITM}{zM} \quad (4)$$

where I is the applied current (A), t is the treatment time, M is the molar mass of the electrode material ($M_{\text{AL}} = 26.982\text{ g/mol}$, $M_{\text{FE}} = 55.845\text{ g/mol}$, z is the valency of ions of the electrode material ($z_{\text{AL}} = 3$, $z_{\text{FE}} = 2$) and F is the Faraday's constant (96485 g/mol). The removal efficiencies (R%) have been calculated with the Equation (5)

$$R\% = \frac{c_0 - c_1}{c_0} \times 100 \quad (5)$$

where c_0 and c_1 are pollutant concentrations before and after EC treatment, respectively. Hydraulic retention times (HRT, min) were calculated with equation (6)

$$HRT = \frac{V}{Q} \quad (6)$$

where Q is the flow rate (liter/min) and V is Volume of water (liter) The electrical energy consumption (EEC, kWh/m^3) has been calculated with the equation (7)

$$EEC = \frac{UIt}{60V} \quad (7)$$

where U is the applied voltage (V), t is the treatment time (min), and V is the volume of the treated water (m^3). Operating cost (OC, THB/ m^3) have been calculated with the equation (8)

$$OC = a \times EEC + b \times EMC \quad (8)$$

where a and b are the current market price of electricity (THB/kWh) and electrode materials (THB/kg), respectively. The EMC (kg/m^3) is the electrode consumption.

3. Experimental

The electrocoagulation treatment is composed of electrocoagulation reactor, power supply and boost converter, ammonia with pH, temperature sensor, microcontroller, nursery pond and sedimentation tank as shown in Fig. 5

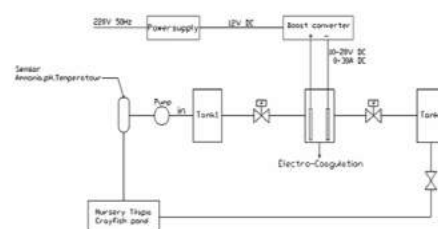
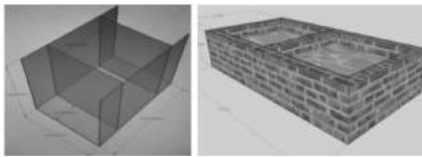
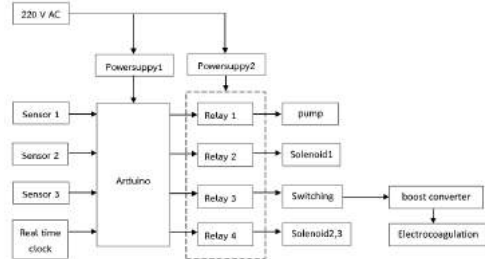
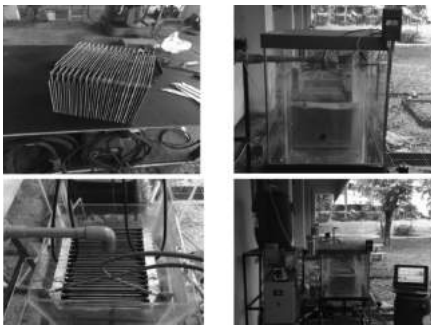


Fig.5 diagram of electrocoagulation system

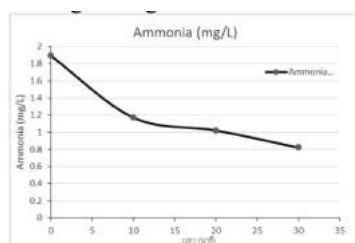
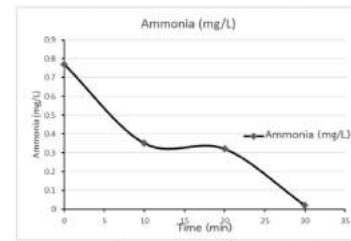
**Fig.6** Chamber of reaction and nursery pond**Fig.7** microcontroller input-output diagram**Fig.8** experimental of electrocoagulation

4. Result and Discussions

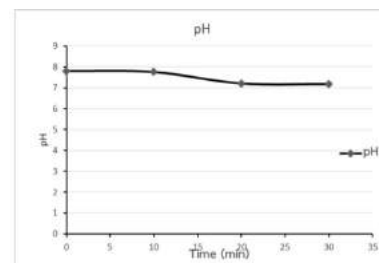
The electrolysis duration is about 30 minutes with DC voltage 10-20 V and current 0-20 V. The result of 2 levels of ammonia intensity removal which composed of 1.89 mg/L and 0.8 mg/L are treated respectively. The physical property of water before and after treatment as shown in Fig. 9

**Fig.9** physical of water after treatment

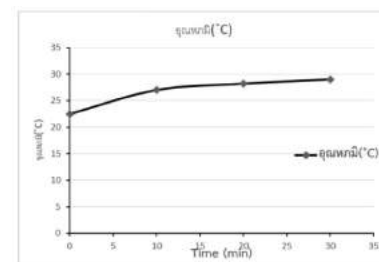
The result of water treatment from ammonia content in water which time as shown in Fig.10-Fig.16

**Fig.10** ammonia content from 1.9 mg/L at different reaction times**Fig.11** ammonia content from 0.78 mg/L at different reaction times

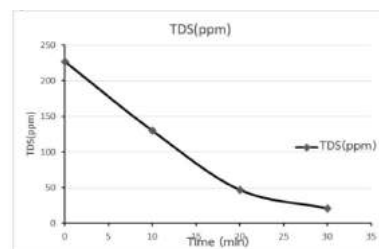
From Fig.10 and 11 the ammonia before treatment is about 1.8 mg/L to 0.8 in 30 minutes and finally decrease less than 0.1 mg/L in 10 minutes respectively.

**Fig.12** pH at different reaction times

From fig 4.8 pH before treatment is about 7.5-8 and pH is constant after treatment until 30 minutes.

**Fig.13** Temperature at different reaction times

From Fig. 13 Temperature before treatment is approximately 23-24 celsius and after that temperature has increase until 29 celsius at 30 minutes of reaction time which cause from heat dissipation from power supply.

**Fig.14** TDS at different reaction times

From Fig 4.5 TDS before treatment is about 225-250 mg/L and TDS is decrease to 25 mg/L at 30 minutes.

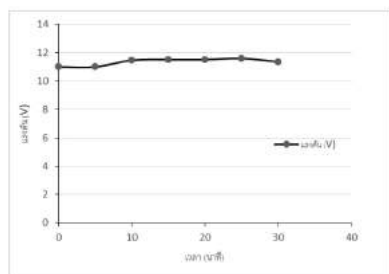


Fig.15 Voltage level of electrocoagulation

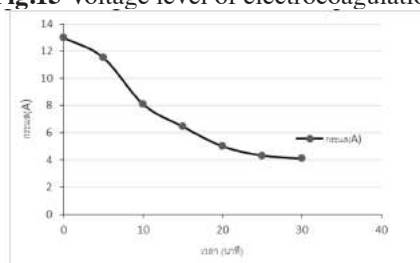


Fig. 16 Current level of electrocoagulation

The energy consumption of reaction times is about 74.47 Wh in duration of reaction time 30 minutes for treat water 5 liters.

5. Summary

In this experimental, the electrocoagulation method which based on electrochemistry principle is presented for ammonia removal. The two of aluminum electrodes are used to be an anode and cathode which receive direct current positive and negative to electrode respectively. An oxidation-reduction (redox) reaction has impact to aluminum ion separation, flocculation, floatation and sedimentation with ammonia particle. The input parameter of this reaction such as types of electrodes, area of electrodes (cm^2), voltage level (V), magnitude of current (A) and current density (A/cm^2) are studied. The output parameters of reaction such as TDS, EC, pH and ammonia intensity are focused. The economic aspect is concerned in term of energy cost and corrosion of aluminum material quantity. The result found that electrocoagulation method can remove ammonia intensity from 1.8 mg/L to 0.8 in 30 minutes and from 0.8 to 0.05 mg/L in 30 minutes for 10 liters reactor chamber by using energy consumption 3.75 kWh/ m^3 or 15 bath/ m^3 .

6. Acknowledgement

The researcher would like to thank Faculty of Science, Rajamangala University of Technology Lanna for support water instrumentation.

7. References

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