# Multi-media filtration for pollutant removal in mud crab hatchery wastewater

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# Abstract

Aquaculture wastewater consists of uneaten fish feed, faeces other excrement and chemical waste. Discharge of aquaculture wastewater directly into the water stream without treatment can harm the ecosystem. Thus, this study aimed to develop a low-cost filtration system for the treatment of mud crab hatchery wastewater. Sponge was used to pre-treat the wastewater mainly to remove larger particles and suspended solids. Sand and zeolite (with and without heat treatment) were used as filter media for the treatment process. FTIR and SEM analysis determined the morphology and surface chemistry of zeolite which acted as an adsorbent in this process.

The physical (temperature, TSS and turbidity) and chemical characteristics (pH, ammonia, TDS and DO) of raw wastewater were determined. The removal efficiency of pollutant for each media used in the filtration system was assessed. From observation, it showed that filter media with heat treatment induced better pollutant removal compared to untreated media. It successfully removed TSS, ammonia and turbidity of wastewater around 18.8%, 90.7% and 100% respectively. It was concluded that the filtration media with heat treament is needed for better pollutant removal in the mud crab hatchery wastewater.

Keywords: Sand, zeolite, ammonia, crab hatchery.

# Introduction

Aquaculture industry has experienced tremendous growth over the last 50 years, from less than a million tons in the early 1950s to over 50 million tons today. Aquaculture in Malaysia has significantly grown from a small-scale familyoriented business to a large-scale operation<sup>10,16</sup>. This growing industry generates nutrient-rich wastewater such as ammonia, nitrates, phosphates and organic load<sup>8</sup>.

The primary sources of ammoniacal nitrogen in aquaculture pond are nitrogen excretion of aquatic organisms and degradation of feed and faeces by microorganisms. In fact, it is also introduced in aquaculture production ponds through nitrogen fertilisers such as ammonium sulfate, ammonium phosphate and urea hydrolysed in ammoniacal nitrogen and watershed runoff<sup>3</sup>.

Furthermore, disparities in aquaculture growth among aquaculture countries have been observed for many years. Due to the increasing market value and high demand of this product, most crab farmers target seeds from the wild to be stocked in the ponds<sup>5</sup>. Current prices of mud crabs in the local market are relatively higher than fish and molluscs which are projected to increase in the world market. This increasing trend in the domestic and export markets is expected to escalate the demand for crab seeds. As a result, mud crab is one of the highest in demand in Asia and other countries owing to high population.

Generally, aquaculture production depends on fingerling, feed, farming areas, climatic factors, farming systems, management practices, market factors, social environment and institutions. Increasing the input factor will increase the aquaculture output. The outputs from feed waste, faeces and pathogens may cause negative externalities among producers, aquaculture industry and other parts of the economy. Differences in input factors in aquaculture production may be the reason for growth disparities.<sup>14</sup>

Therefore, intensive conservation of aquatic species should be performed while minimizing the associated negative impacts including removal of excess dissolved nitrogen (DN) from wastewater<sup>12</sup>. A large amount of DN in aquaculture wastewater occurs in inorganic form. Waste and natural food are the only sources of nutritional inputs for farmed aquatic organisms before the relatively recent and increasing use of pellet feed in modern aquaculture leading to primary environmental concern<sup>17</sup>. More recent studies have reported that 25% of feed used in the aquaculture system would end up as suspended solids<sup>1</sup>.

Wastewater generated in the aquaculture industry needs treatment before being reused or released into the environment to avoid eutrophication. Ammonia and nitrite can be toxic to aquatic life in aquatic systems<sup>11</sup>. Despite the presence of free ammonia, anaerobic digestion of fish sludge to produce biogas is a promising approach to reduce the environmental impacts of fish sludge treatment by recovering energy through biogas production while removing COD and BOD<sup>13</sup>. Levels of free ammonia in fish sludge can inhibit anaerobic digestion, but aquaculture

effluents can be diluted or mixed with other substrates to enhance digester performance<sup>15</sup>.

Maintaining water quality and stabilising water parameters are among the greatest concerns encountered by the aquaculture industry. A healthy aquatic environment is essential for the aquacualture farming industry. For a positive aquaculture development, effluent or wastewater treatment methods such as membrane filtration must be upto-date in terms of their activities, costs and operational skill requirements<sup>4</sup>. Nowadays, low-cost adsorbents such as zeolite for water treatment are highly desirable. Zeolite has also been used to remove ammonia nitrogen from wastewater<sup>18</sup>. In aquaculture, zeolites are associated with the control of total ammonia nitrogen (TAN) concentration which is the main interest.

Ammonia is toxic to fish, shrimp and other aquatic animals. The zeolite is used to reduce TAN concentrations in aquariums, fish holding tanks, aquaculture water recirculating systems and water containers to transport aquatic animals<sup>9</sup>. Ammonia removal by zeolite is possible as ammoniacal nitrogen exists as ammonium  $(NH_4^+)$  and ammonia  $(NH_3)$  in the following pH and temperature equilibrium<sup>19</sup>:

 $NH_3 + H_2O = NH_4^+ + OH^-$ 

The proportion of ammonium decreases with increasing pH but even at pH 9.0, ammonium comprises about 70% of

ammoniacal nitrogen in the water. The removal of ammonia by zeolite will lower the TAN concentration and will reduce the ammonia concentration at equilibrium. Therefore, this study aimed to provide valuable information on the effectiveness and stability of multi-media filtration system in treating aquaculture wastewater from mud crab hatchery. Sand and zeolite with and without heat treatment were used as filter media. Treated and untreated zeolites were characterised in terms of morphology and surface chemistry using Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy respectively.

The quality of the treated wastewater was determined in terms of turbidity, ammonia and total suspended solid (TSS) removal efficiency. Dissolved oxygen concentrations were also determined before and after the fitration treatment.

### **Material and Methods**

All materials used in this research were obtained from Hutan Lipur Lata Payung. Zeolite and sponge were purchased from a convenience shop around Gong Badak, Kuala Terengganu. Heat treatment of zeolite was carried out at a rate of 2°C/min at room temperature and then stored at temperature of 240°C for 6 hours, then cooled to 30°C at a rate of 2°C/min. Heat treatment for sand was also carried out in an oven for 1 day at temperature of 180°C. All media/materials used were analysed in terms of pore size or other characteristics. Biofilters were used and characterised using FTIR and SEM.

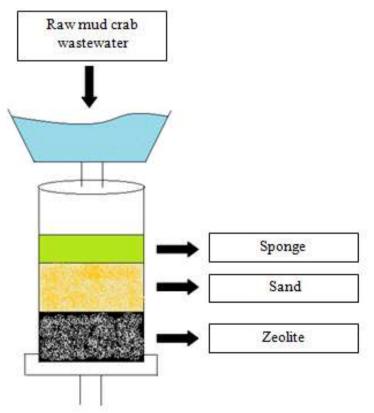


Fig. 1: Design of filtration system

Fig. 1 depicts the design of filtration system used in this study. First, the wastewater was filtered with a sponge followed by heat-treated sand and zeolite media. For control, the analysis was also repeated using the untreated media with similar sequence of sponge, sand and zeolite. The analysis was repeated twice to obtain the average reading value.

Wastewater was analysed in terms of temperature (°C), pH, dissolved oxygen (DO) (mg/L), total dissolved solid (TDS) (mg/L), total suspended solids (TSS) (mg/L), ammonia (NH<sub>3</sub>) (mg/L) and turbidity (NTU) using multiparameters. For removal efficiency, the calculation was conducted using the formula below where Cinitial and Cfinal represent initial and final parameters such as ammonia, TSS and turbidity respectively.

Removal efficiency =  $\frac{C_{initial} - C_{final}}{C_{initial}} X 100$ 

### **Results and Discussion**

Characterisations of Zeolite: SEM micrographs of untreated and treated zeolites are shown in fig. 2 (a) and (b) respectively. The morphology images obtained from SEM exhibited an irregular fibrous morphology with angular reliefs and small deformations caused by the zeolite melioration process. According to the images obtained, pores did not appear, may be because the surface of the carbonaceous material was not flat enough to permit light to pass through. The SEM image of the untreated zeolite in fig. 2(a) showed that the pore size of the zeolite was 0.370 µm.

The surface morphology was observed to be rougher with coarse grains, creating a large contact area. Zeolite obtained after heat treatment in fig. 2(b) exhibited agglomerated structure. This indicated that the pore size was different and larger in size. Moreover, many large pores indicated the intense densification of polymer blend at elevated temperature.

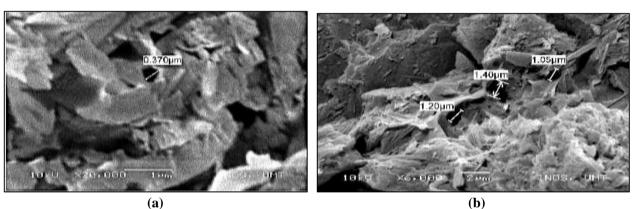
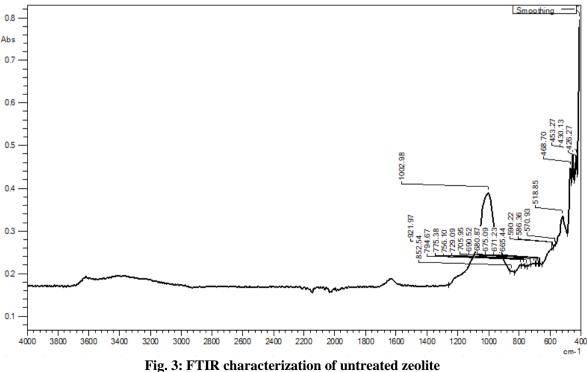


Fig. 2: Images of zeolite (a) without heat treatment and (b) with heat treatment analysed by SEM



SEM image of treated zeolite showed pore sizes of 1.40  $\mu$ m, 1.20  $\mu$ m and 1.05  $\mu$ m. An increase in the number of large pores may be favourable to a decrease in support resistance. However, this was unfavourable to the increase in the mechanical strength of the supports. In addition, the heating process also helped create small particles with large surface areas. Heat treatment at 270°C also improved the flux of the zeolite membrane where the pores of the supports became too large and the mechanical strength of the membrane decreased. Heat treatment longer than 12 hours at 240°C increased the pure water flux of the supports but decreased the flux of the zeolite membrane in pervaporation. This is consistent with the SEM results suggesting that large pores were produced probably due to the appearance of tiny pores.

The untreated zeolite was characterised using FTIR in the range of 4000–400 cm<sup>-1</sup> as displayed in fig. 3. The IR showed a strong intensity adsorption band at 1002 cm<sup>-1</sup> and 518 cm<sup>-1</sup> due to the presence of C-F and C-Br respectively in alkyl halide group-stretching vibration<sup>6</sup>. Wavelengths at 794 (C-Cl), 468 and 453 cm<sup>-1</sup> were associated with C-I in alkyl halide group-stretch vibration with strong intensity. Meanwhile, peaks at 921 cm<sup>-1</sup> and 852 cm<sup>-1</sup> indicated the presence of C-H in alkene group-bending vibration with strong intensity.

The Effects of Treated and Untreated Filter Media on Pollutant Removal: The effects of different types of untreated and treated filter media were investigated with parameters such as pH, temperature, ammonia, dissolved oxygen, TDS, TSS and turbidity. The removal efficiency (%) of parameters was also investigated.

According to the results in fig. 4, the removal efficiency of ammonia was gradually increased. The percentage removal efficiencies of ammonia using treated sand and zeolite were 80.70% and 90.70% respectively. However, the untreated sand and zeolite have lower removal efficiencies of 57.44% and 62.33% respectively. These may be because sand and zeolite have undergone heat treatment and have larger pore sizes to absorb ammonia as shown in fig. 2(b).

Zeolite comprises aluminosilicates with a three-dimensional structure consisting of AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra which are linked by an oxygen atom. This wide-open and stable structure contributes to better removal efficiency. This effect results in higher cation exchange capacity and cation selectivity, higher void volume and greater affinity for cation ions such as  $NH_4^+$  and other types of organic ions with positive charge<sup>7</sup>. Similar results and trends are also reported by Hamzah et al<sup>11</sup> where 79% ammonia removal was achieved using thermal decomposition of hydroxyapatite (Hap).

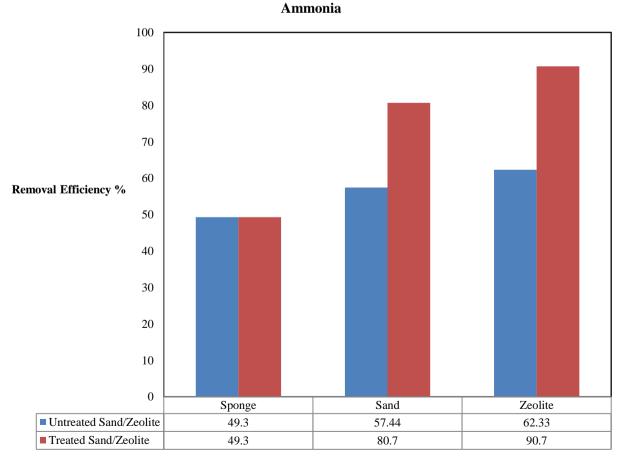
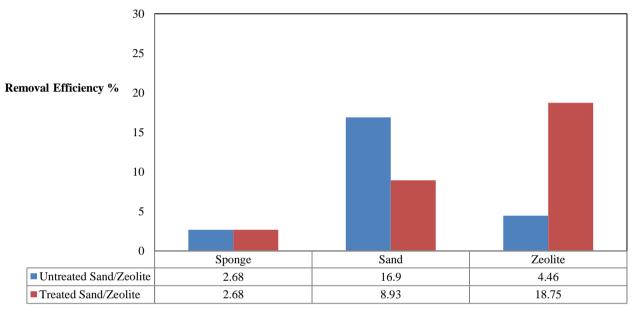


Fig. 4: Removal efficiency of ammonia on untreated and treated filter media

Based on fig. 5, the removal efficiency of TSS for the untreated media was higher for sand (16.90%) compared to zeolite with only 4.46% TSS removal. This could be due to dust particle mixed with the sand acting like a sand filter. The untreated sand contained small dust particles causing results instability. The treated zeolite filter media showed a better TSS removal efficiency of 18.75%. Compared to treated zeolite, treated sand filter media exhibited much lower removal efficiency of 8.93%.

The reason may be because the treated sand has fewer dust particles and indirectly increased the percentage removal. These values obtained proved that the treated filter media could reduce TSS and purify water in a better way.

Fig. 6 shows the turbidity removal of untreated and treated filter media. Sponge was found to be able to filter largersized particles by 64.29%. The removal efficiency of turbidity was 100% for treated sand and zeolite signifying that the final turbidity recorded was zero. The treated filter media has higher turbidity removal efficiency compared to the untreated filter media, namely 85.71% and 71.43% for sand and zeolite respectively.



**Total Suspended Solid** 

Fig. 5: Removal efficiency of total suspended solid (TSS) on untreated and treated filter media

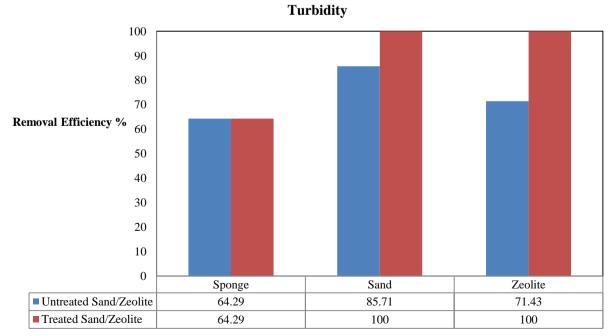


Fig. 6: Removal efficiency of turbidity on untreated and treated filter media



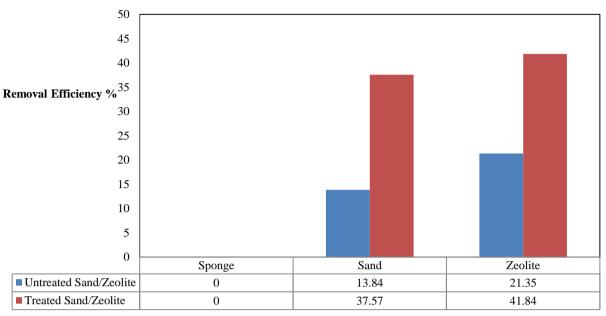


Fig. 7: Removal efficiency of dissolved oxygen on untreated and treated filter media

These results demonstrated that the treated media were more effective than the untreated media due to the highest turbidity removal.

Fig. 7 shows the removal efficiencies of DO. The highest removal efficiencies were obtained by the treated sand and zeolite of 37.57% and 41.84% respectively. Similar to the previous turbidity and ammonia parameters, the removal efficiencies of untreated sand and zeolite were lower at 13.84% and 21.35%. The higher removal efficiency for ammonia and turbidity was related to the DO. When DO is higher, more oxygen is generated which is beneficial for aquatic system.<sup>2</sup>

## Conclusion

The effect of heat treatment on filter media was studied. Treated and untreated filter media, namely sand and zeolite were examined for ammonia, DO, TSS and turbidity removal from mud crab hatchery wastewater. The results showed a positive trend when using treated sand and zeolite as potential filter media for pollutant removal from mud crab hatchery wastewater. For all parameters, the treated filter media were improved by at least 50% removal efficiency. The average removal efficiencies of TSS, ammonia, and turbidity of wastewater were 18.8%, 90.7% and 100% respectively.

For performance evaluation, the filter media with heat treatment were more effective to remove ammonia in wastewater compared to untreated media. Heat treatment at 270°C also improved the flux of zeolite membrane. For a better future of the aquaculture industry, heat-treated sand and zeolite are needed for a sustainable and eco-friendly wastewater quality.

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