Determination of Efficiency of Crab Shell Powder for the Treatment of Fish Waste Water

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Introduction

Water is the most important and basic requirement for life on earth. However, only about 1% of the world's water can be used for the human consumption. Seafood processing is one of the major industry, which threatens the quality of natural water bodies due to its composition (Zvezdov and Zvezdova, 2010). It elevates the Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), Fats, Oil and Grease (FOG) in natural waters and causes eutrophication (Tahir *et al*., 2013). Some toxic residues may be produced as by-products due to chemical reagents used in conventional wastewater treatment methods, which are toxic for human health and the environment (Gaherwar and Kulkarni, 2012). Hence the utilization of shellfish waste has been proposed as a low cost and eco-friendly wastewater treatment method to solve environmental problems and as a waste management alternative to the masses of shellfish wastes (Muhaemin, 2005). Shells of *Portunus pelagicus* were used in this study to examine its effectiveness as an adsorbent in treatment of fish processing wastewater.

Methodology

Crab shells collected from Alpex Marine (pvt)were cleaned and dried at 100 °C for 8 hours using MICHCHEL tray dryer and crushed then sieved to raw powder with 0.1-0.5mm particle size range.50 g of raw powder was heated at 950 °C for three hours in a muffle furnace (Xy-1100x-L) to prepare heat treated crab shell powder. Chitin and Chitosan were collected from Industrial Technology Institute laboratory. Wastewater samples were collected from Ceylon Fresh Seafood(pvt) and initial COD (Golterman and Clymo, 1970), pH, temperature (MARTINI pH 55 pH meter), Total Dissolved Solid (TDS) (EUTECH CON 510 TDS meter) and turbidity (TN-100 turbidity meter)values of the wastewater were recorded.

The first experiment was done to find out best powder dosage and 5.0 gl $^{-1}$, 1.0 gl $^{-1}$ and 0.5 gl $^{-1}$ dosages were taken from each powder type then placed into 250 ml glass beakers. Then 100 ml of fish wastewater was added to each beaker and stirred for 2 minutes Three replicates were used for each treatment. A beaker containing wastewater only was used as the control. After 24 hours final pH, temperature, TDS, turbidity and COD of treated wastewater were measured using AOAC (1985).

During the second experiment initial pH value of the wastewater samples were adjusted to pH 5, 7 and 9 by adding 0.1 M HCl or 0.1 M NaOH. Then selected the best powder dosage from the experiment 1 was used for the second experiment and same procedure was followed to find best pH value which allows highest COD reduction.

In the third experiment pH of the wastewater was maintained at the best pH value which was selected from the second experiment. Combinations of Chitosan and heat treated crab shell powder was used in1:1, 1:2, 1:3, 3:1 and 2:1 ratios. Total powder weight in each combination was equal to the best powder dosage which was selected from the first experiment. After 24 hours same procedure was followed as in the early experiments. Finally best powder combined ratio was selected based on highest COD reduction.

Significant effect of each treatment was analysed by analysis of variance (ANOVA) using General Linear Model (GLM) procedure of Minitab 16 statistical package.

Results and Discussion

According to the results, treatment type and powder dosage had a significant effect ($p<0.05$) on COD reduction. Experiment 1, heat treated powder and chitosan at 0.5 gl^{-1} and 1.0 gl^{-1} dosages, showed significantly ($p>0.05$) higher COD reduction than other treatments. Accordingly both Chitosan and heat treated powders were selected for the third experiment. Similar finding have been observed by Tsonis *et al.* (1989), Zvezdov and Zvezdova (2010), Geethadevi *et al.* (2013) and Geethadevi *et al.* (2012). Chitin and raw crab shell powder did not show good performances in reducing COD. It is a deviation from the findings of Kim and Park (2001)and Chui *et al.* (1996). Heat treated powder has shown significantly ($p>0.05$) higher pH, TDS and turbidity increments. Muhaemin (2005) also described that, pH of the solution with heat treated crab shell shifted rapidly up to 10 within 20-30 minutes before reaching a stable value.

Considering the cost effectiveness 0.5 gl^{-1} was selected as the best powder dosage for the second experiment. The charge density increased with increase in powder dosage and hence increases in adsorption rate. The excess dosage has the possibility to get a charge reversal, which led to particle re-stabilization and it can create additional COD in the solution (Geethadevi *et al*., 2013and Geethadevi *et al*., 2012).Therefore, it was crucial to determine the optimum powder dosage to minimize the cost and increase effectiveness. pH and TDS were increased with increasing powder dosage. 1.0 gl^{-1}powder dosage show higher turbidity than 5.0 gl^{-1} and 0.5 gl^{-1}powder dosages. It is a deviation from the results of Geethadevi et al. (2013) and Geethadevi et al. (2012).

In the experiment 2, the highest COD reduction was shown by chitosan at pH 5.Increment of pH up to 7 and 9, the effectiveness of the chitosan has gradually decreased. Geethadevi et al. (2013) and Geethadevi et al. (2012) pointed out that there are 90% of the functional groups of NH_2 on chitosan surface that has been protonized at pH 4 and gradually decrease as solution pH increases. Heat treated crab shell powder effectively absorb effluents at pH 9 but its effectiveness not much affected by pH reduction. Jatto *et al.* (2013) also described that crustacean shell is very stable in both acidic and alkaline medium.

pH increment is reduced and turbidity increased with increasing pH value. Temperature and TDS are decreased at neutral pH. Turbidity increment observation is in agreement with the findings of Geethadevi et al. (2013) and Geethadevi et al. (2012), but TDS reduction observations have deviated from those findings.

The highest COD reduction was shown by chitosan and heat treated powder at 3:1 ratio in the experiment 3.This finding is similar to the observations of Geethadevi *et al.* (2013) and Geethadevi *et al.* (2012) where they clearly demonstrated that the effectiveness of Chitosan was maximum at pH 4-5. Chitosan: heat treated powder with 1:1, 1:2, 1:3ratios did not show any significant difference ($p>0.05$) with the Chitosan: heat treated powder 3:1 ratio. According to Muhaemin (2005), Zhou *et al.* (1999) and Jatto *et al.* (2013) high amount of OH ions present in the solution can reduce the COD by precipitation of organic matters. Preparation of heat treated powder was cheaper than the production of chitosan. So that, Chitosan: heat treated powder 1:3 ratio can be used as the most cost effective treatment.

Conclusions

Crab shells effectively reduced the COD in fish wastewater. Selection of best powder dosage and pH value is important to achieve highest absorption efficiency. Although a significant deviation in COD reduction was observed between four powders, Chitosan and heat treated crab shell powder still exhibited a good COD reduction capacity. This becomes a waste disposal alternative to the crab shells from processing plants and crab shells are 100% environmental friendly materials which can replace the chemical treatment methods.

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