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Fish aquaria studies on control of chloride salinity through formic acid applications

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Abstract
The objective of the present study was to apply certain chemical means for reducing chloride salinity levels in aqueous medium. For this purpose, the excess chlorides were controlled through chemical applications using formic acid in the presence of *Labeo rohita* fingerlings in aquarium environment. The effects of this particular chemical on the water quality as well as on fish survival and growth parameters was also studied. The results indicated that formic acid was not found much effective in reducing chloride salinity levels to appreciable limits, however water quality was not much affected by its usage. The fish growth and survival rates were also found non-satisfactory and higher doses resulted in toxic effects on these parameters. The results of all these efforts concluded that the use of this chemical for chloride salinity reductions should not be recommended.

Keywords: Chloride reductions, formic acid, *Labeo rohita*, water quality parameters

1. Introduction
Fish is a cheapest source of protein and an important cash crop which carries out all their life functions such as feeding, swimming, breeding, digestion and excretion in water media [1]. The physico-chemical parameters of water such as dissolved oxygen, carbon dioxide, pH, temperature, total alkalinity, total hardness, chloride concentration, electrical conductivity and salinity directly affect the life functions of fish. Disturbance or imbalance of any of these parameter directly or indirectly causes the mortality of fish [2]. Tolerable limits of these water quality parameters in which the fish perform optimally are different. It depends on the age and size of fish. Any increase decrease of these physico-chemical parameters tolerable limits causes the adverse effect on the fish health [3, 4].

Chloride as Cl^- ion, is one of the dominant inorganic anion of saltwater and freshwater that emerges from the dissociation of salts in water (originating from sodium chloride, calcium chloride, magnesium chloride, natural minerals, saltwater, manmade salts and industrial pollution) and contributes to elevated chloride readings in fish pond. Chlorinated drinking water and sodium chloride water softeners may often increase chloride levels in water. There are some locations in Punjab region, Pakistan whose water bodies have been diagnosed with high chloride salinity level that can interfere with the optimum growth of the fish in aquaculture in those particular areas especially the salt range areas [5, 6]. There is no direct method to control high quantities of chloride ions. Previously, sulphur-based chemicals were used to control the quantity of chloride in fish pond but sulphur-based chemicals are oxygen scavengers and lower the dissolved oxygen in fish pond, and some sulphur compounds are also hazardous chemicals [7, 8], hence, these are not recommended chemicals.

Formic acid, a reducing carboxylic acid, is a colorless liquid with a pungent odor and a volatile reducing agent, however, its volatility is rather low. Its principal use is as a preservative and antibacterial agent in livestock feed. When sprayed on fresh hay or other silage, it arrests certain decay processes and causes the feed to retain its nutritive value longer [9]. In the present study, formic acid was applied with different concentrations in aquatic media having fish species to determine the chloride reduction levels, effects on physico-chemical parameters along with study on fish growth and survival rates.

2. Materials and Methods
2.1 Experimental Layout
The present experiment was performed in chemistry laboratory, FR&TI, Lahore for 31 days duration from 1st March, 2017 to 31st March, 2017.

There were six treatments including control with triplicates for each. 18 glass aquaria with 40 litre water fillings were used for each trial. About 40 g commercial sodium chloride was added to each aquarium for preparation of saline water. Five different doses of formic acid i.e. 10 ml of 2.5% / 40L, 10 ml of 5.0% / 40L, 10 ml of 7.5% / 40L, 10 ml of 10.0%/ 40L and 10 ml of 12.5% / 40L were applied in the liquid form with constant stirring. The chloride concentration was recorded before and after the application of chemical; the same test was performed daily for one month period to check the effectiveness of the particular chemical. The fingerlings of *Labeo rohita* were procured from Chhenawan Fish Hatchery, Punjab. Ten fingerlings were stocked in each glass aquarium containing the saline water. Regular aeration was done for the maintenance of optimum level of dissolved oxygen in saline water. The fish mortality was also recorded to observe the chemical effects on fish.

2.2 Water quality analysis
The water quality analysis was done before and after the application of each dose of chemical under observation. Dissolved oxygen, pH and electrical conductivity were monitored through digital meters. The chloride concentration, free carbon dioxide, carbonate alkalinity, total alkalinity and total hardness were monitored by titration methods following the protocol of APHA [10].

2.3 Statistical analysis
The statistical analysis following Steel *et al.* [11] on SPSS (Version 22) was applied to find the significant differences for chloride level changes through application of formic acid.

3. Results and Discussion
All the results are presented in the shape of bar and trending graphs.

3.1 Effect on chloride level reductions
Fig 1 shows the differences in the decrease of chloride level by applying five doses in the treatments (T2, T3, T4, T5 and T6) along with one control. After the addition of afore mentioned doses of formic acid, the average value of chloride level remained up to 481 to 505 mgL^{-1} in T6, T5, T4, T3 and T2, respectively during experimental period. These values gradually decreased within one month span and it was also observed that the decreased level of chloride level became constant with the passage of time. Fig 2 shows the trending changes in the decrease of chloride level through the use of chemical with the passage of time. The initial maximum chloride levels were 511, 510, 509, 508, 507 and 510 for T1, T2, T3, T4, T5 and T6 while after application of chemical in 31 days' time duration, these values decreased and reached up to 497, 489, 484, 487, 484 and 481, respectively. The chemical was not applied to T1 treatment. The analytical analysis revealed that the results were not significant with each other and this chemical application was not much effective for reduction of chloride salinity concentrations up to satisfactory levels.

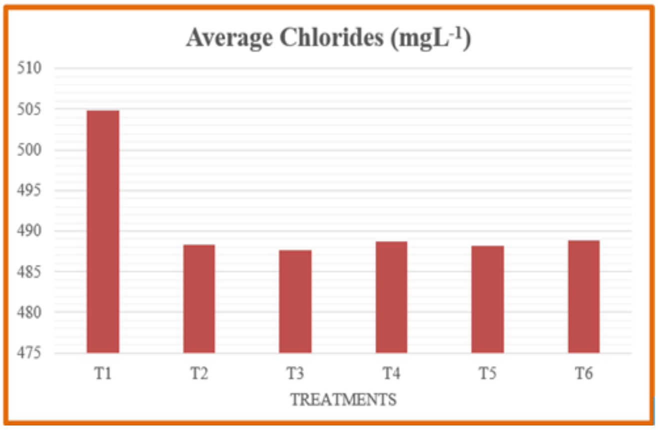

Fig 1: Comparative average chlorides (mgL^{-1}) in all treatments

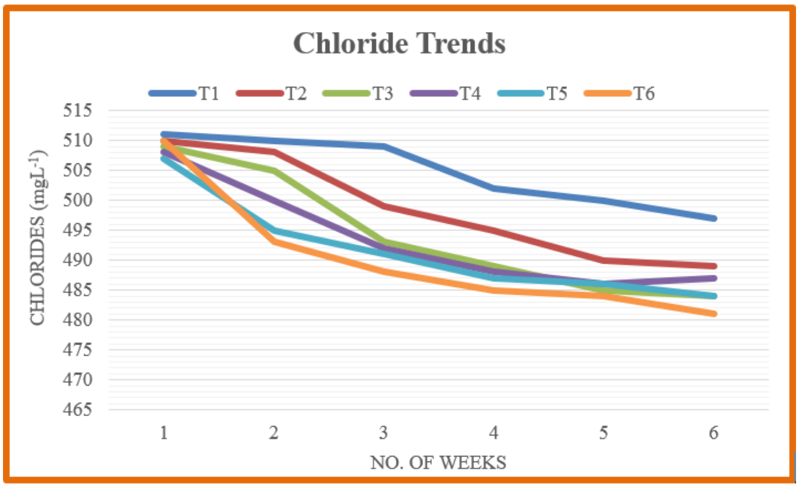

Fig 2: Comparative average chloride trends (mgL^{-1}) trends in all treatments

3.2 Effect on weight, length and survival of fish species
Fig 3, 4 and 5 shows the comparative average weight, length and survival Comparison of *Labeo rohita* fingerlings. Results showed that the increase in the amount and concentration of formic acid gradually decreased the weight, length and survival rate of fish. As far as the mortality of fish was concerned there was no mortality of fish observed after the addition of the five different doses of formic acid in the treatments TI, T2, T3, T4, T5 and T6 at the initial stages. Whereas the same was observed during the next ten days trial in all treatments. However, after 10 days and up to 31 days, the % age survival rate of fish fingerlings remained up to 83%, 76%, 56%, 36%, 25% and 13% in the treatments TI, T2, T3, T4, T5 and T6, respectively. From this, it can be deduced that although chloride concentrations were reduced by the application of chemical, however, it was not found favourable in the presence of the fish species under observation since it reduced the growth and survival parameters which can be clearly observed through the already mentioned figures.

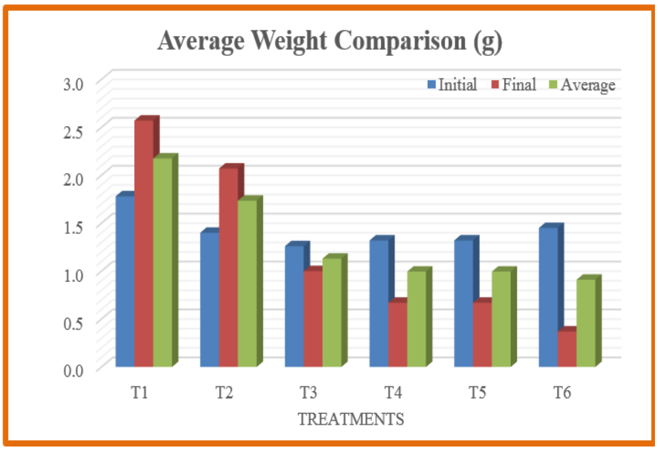

Fig 3: Comparative average weight comparison (g) in all treatments

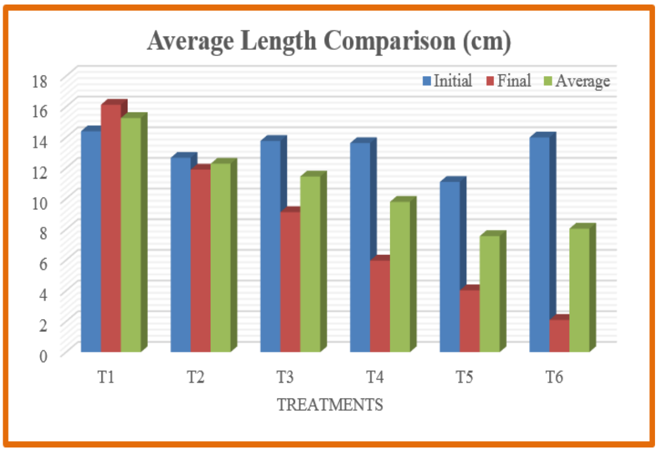

Fig 4: Comparative average length comparison (cm) in all treatments

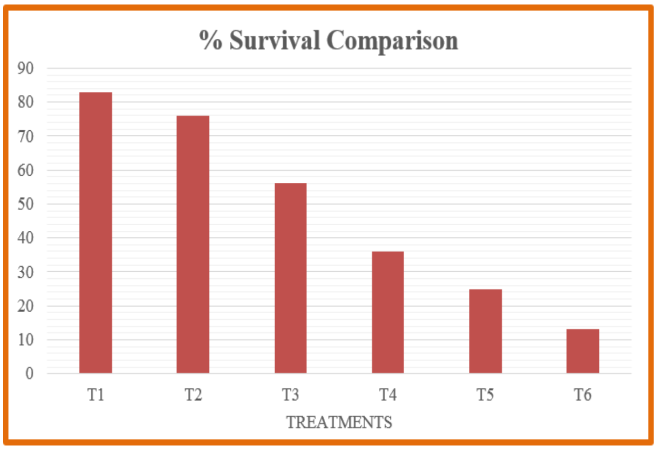

Fig 5: Comparative % survival comparison in all treatments

3.3 Effect on water quality

The results on average temperature, dissolved oxygen, pH, electrical conductivity, total dissolved solids, carbonate alkalinity, total alkalinity and total hardness have been shown in Fig 6 to Fig 13, respectively. The carbon dioxide was found Nil in all the treatments. The average temperature remained minimum at 30.7 °C and maximum up to 30.8 °C for all the treatments. The average dissolved oxygen remained between 3.75 to 3.80 mgL^{-1} for all the treatments. The average pH values were found to be 8.3, 7.9, 7.7, 7.4, 7.1 and 6.7 for treatments TI, T2, T3, T4, T5 and T6, respectively. The average conductivity was observed between 2148.33 to 2187.66 µS cm^{-1} for all the treatments. The average total dissolved solids were between the range 1826.08 to 1858.67 mgL^{-1} for all the treatments. The average carbonate alkalinity was from 38.0 to 38.17 mgL^{-1} while the average total alkalinity was between 415.33 to 416.50 mgL^{-1} for all the treatments. The average total hardness remained between 181.00 to 207.50 mgL^{-1} for all the treatments. All the parameters remained within the suitable limits required for any fish aquaculture system and no abrupt changes were observed during the whole trial period which is evident from the below mentioned results.

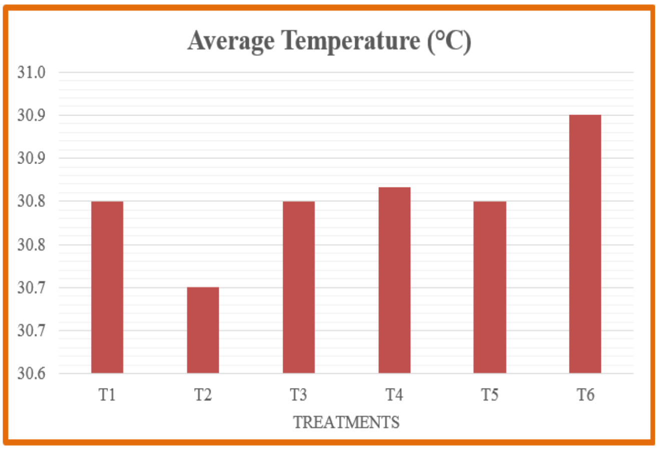

Fig 6: Comparative average temperature (°C) in all treatments

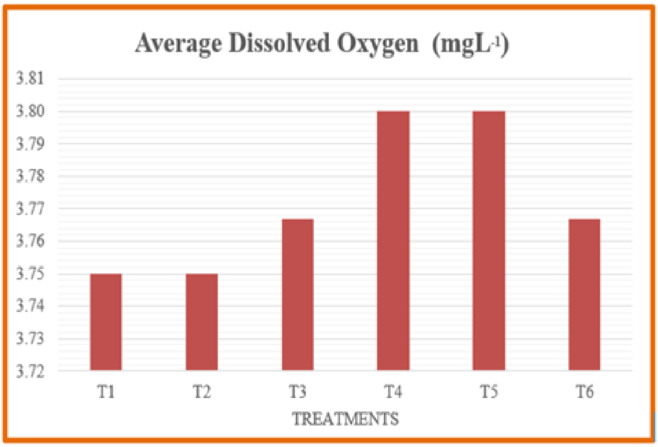

Fig 7: Comparative average dissolved oxygen (mgL^{-1}) in all treatments

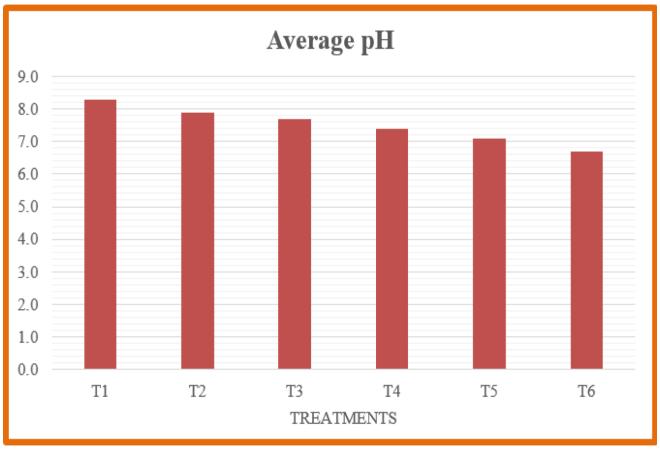

Fig 8: Comparative average pH in all treatments

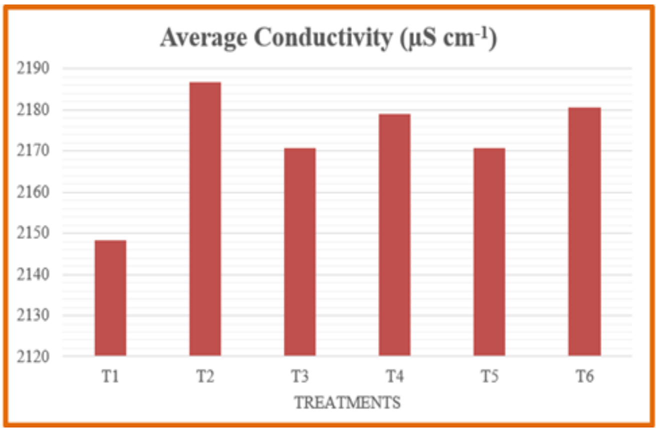

Fig 9: Comparative average conductivity (µS cm^{-1}) in all treatments

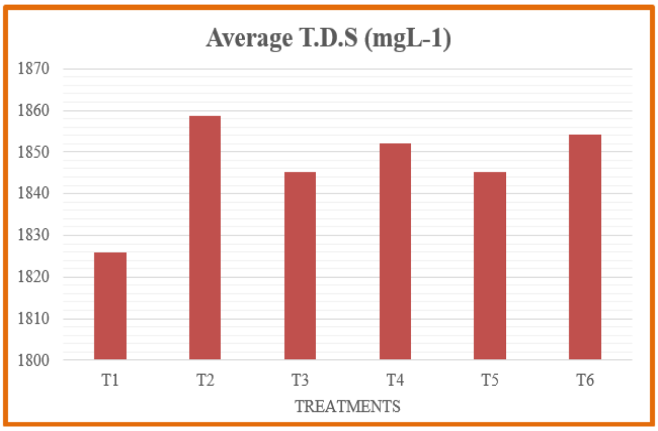

Fig 10: Comparative average T.D.S (mgL^{-1}) in all treatments

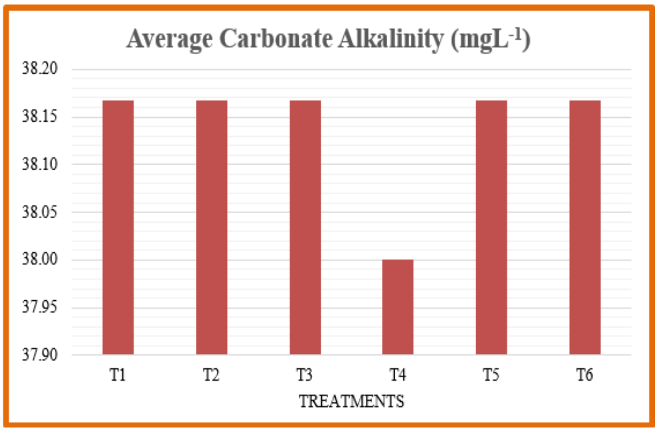

Fig 11: Comparative average carbonate alkalinity (mgL^{-1}) in all treatments

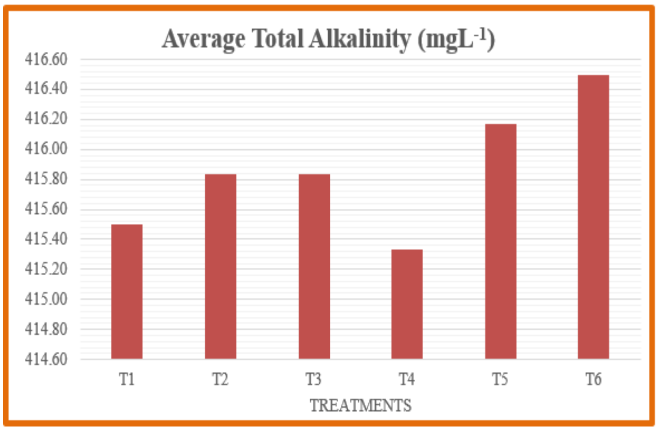

Fig 12: Comparative average total alkalinity (mgL^{-1}) in all treatments

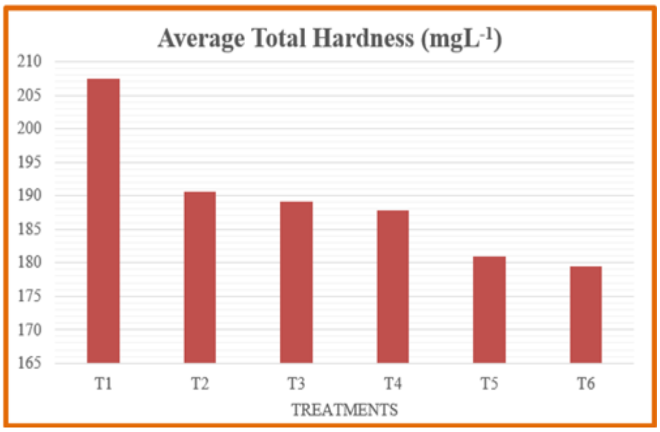

Fig 13: Comparative average total hardness (mgL^{-1}) in all treatments

3.4 Comparative Literature Survey account with present undertaken research

Several research studies have already been undertaken for control and reduction of chloride levels in water containing different fish species with the help of various chemicals. Our results are not in accordance with the studies of Ritter [9] who reported that the natural reducing agents like formic acid, oxalic acid and tartaric acid are non-toxic and can be broken down biologically and manifest a reducing action with regards to chlorine and other active chlorine compounds and applied these for chlorides reduction purposes. Our studies does not support the findings of Hill [12] who studied that the chemical methods of dechlorinating water are faster than the passive methods. Our results are in accordance with the findings of Hall *et al.* [7] who suggested that the chlorinated and sulfonated water poses a hazard to some sensitive aquatic species. Meador and Carlisle [13] also worked on quantifying chloride tolerance indicator values for common stream fish species of the United States. Other methods have also been used previously like Orellan *et al.* [14] who described an electrochemical chloride extraction (ECE) for removal of chloride from a solution of NaCl within 7 weeks and Xuelian *et al.* [15] who used an electrochemical method to remove chloride ions from zinc sulfate aqueous solution using a potentiostatic technique, and using copper sheets as a working electrode and an auxiliary electrode, Ag/AgCl electrode as a reference electrode. Other scientists have also used various chemicals for control of chloride salinity like Arif *et al.* [16] who used many chemicals for this purpose and concluded that Zinc nitrate was the most efficient in removing chlorides then Aluminium hydroxide and Aluminium nitrate while Sodium acetate the least efficient one. They further described that Aluminium hydroxide was found the most effective for fish survival and growth rate while Zinc nitrate remained the least effective one.

4. Conclusion

From the present study, it can be concluded that formic acid was not found much effective in reducing chloride salinity levels to appreciable limits, however water quality was not much affected by its usage. The fish under consideration i.e. *Labeo rohita* growth and survival rates were found to be compromised to some limits with lower chemical doses but higher doses resulted in toxic effects on these parameters. The results of all these efforts concluded that the use of this chemical for chloride salinity reductions should not be recommended.

5. Acknowledgement
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