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Reduction of Ammonical Nitrogen During Shock load in Crude Refining Industry

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Abstract

The Project is based on Reduction of Ammonical Nitrogen from the waste water of Refinery. Where the Shock loads occurs during the leakages, spillages, washing and cleaning of some vessels which leads to high oil content in waste water. During the shock loads the Ammonical Nitrogen value exceeds the design capacity of treatment plant and formed Ammonical Nitrogen goes to the ETP where it is needed to be removed so it becomes inefficient to remove it. Thus we have determined process for the reduction of Ammonical Nitrogen value during the shock loads by studying and working on Breakpoint Chlorination Method. After implementation of Breakpoint Chlorination method the desired results can be obtained which can help the industry to maintain the discharge standards of the final effluent. In this method we even modified the method by varying the pH and temperature for efficient removal. Further study can be done to reduce Ammonical Nitrogen in a more efficient manner by adding different catalyst.

***Key Words**: Ammonical Nitrogen, Break-point Chlorination, shock loads.*

I. INTRODUCTION

Chlorine is the most widely used disinfectant for drinking water and wastewater. It is commonly applied in the form of chlorine gas, sodium hypochlorite solution, or calcium hypochlorite. Chlorine gas is slightly soluble in water [1]. Once it is dissolved in water hydrolysis occurs rapidly.

$$Cl_2 + H_2O = HOCl + H^+ + Cl- \quad (1.1)$$

Nearly complete hydrolysis in a few tenths of a second at room temperature [2]. Sodium and calcium hypochlorite also hydrolyze to form hypochlorous acid. Hypochlorous acid is weak acid [3]. It is partially dissociated to form hypochlorite ion as follows:

$$HOCl = H+ + OCl- \quad (1.2)$$

In water at pH to 8.5, both species are presented to some degree. The sum of HOCl and OCl- concentrations is called Free Available Chlorine or FAC.However, ammonia and organic nitrogen exists in many waters. Chlorine reacts with ammonia and some nitrogenous organics to form a class of compounds called chloramines. Chloramines are characterized by the presence of one or more N-CL bonds. Three type of chloramines can be formed from the reaction of chlorine and ammonia nitrogen.

$$HOCL + NH_3 = NH_2Cl + H_2O \quad (1.3) \qquad HOCL + NH_2Cl = NHCl_2 + H_2O \quad (1.4)$$
$$HOCL + NHCl_2 = NCl_3 + H_2O \quad (1.5)$$

The competition between reactions depends on the pH of the water, temperature, contact time, and most important of all, and the initial chlorine to ammonia ratio[4]. Monochloramine and dichloramine are the two dominant species in most cases. Chlorine reacts with some nitrogenous organic analogously to equation (1.3) or (1.4) too form organic chloramines. The sum of all chloramines is called Combined Available Chlorine available or CAC. The sum of the CAC and FAC is called Total Residual Chlorine (TRC).

The breakpoint curve represents graphically the relationship between the residual chlorine and the added chlorine(chlorine dose). A theoretical breakpoint curve is shown in figure 1.1. In this curve, several characteristic zones can be identifies. The dominant reaction in zone 1 is the reaction between chlorine and ammonia indicted in equation (1.3).

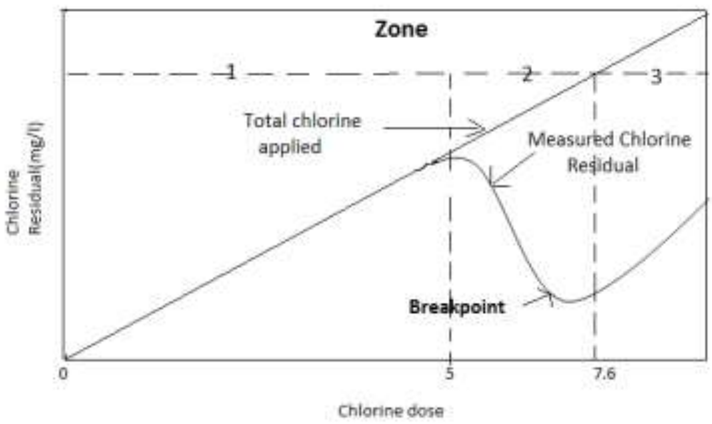

Figure 1.1: Theoretical curve of chlorination to break point[5]

The chlorine residual contains mainly monochloramine. The total chlorine maximum occurs theoretically at a chlorine to ammonia of 5:1 by weight (molar ratio of 1.1).As the chlorine to ammonia molar ratio starts to exceed 1:1, the reaction in equation 2-4 starts and forms dichloramine. Reactions contributes to the breakpoint of chloramines to nitrogen gas as listed in section 3 [7].

The dose at which ammonia has been oxidized completely and the residual chlorine is minimized is called the breakpoint .The theoretical chlorine to ammonia weight ratio at the breakpoint is 7.6. At this point, most chloramine are oxidized, and a very low chlorine residual remains in the water.

The dominant residual existing in the water in zone 3 is free chlorine. Only small amount of dichloramine and trichloramine can be found. An increase in the chlorine dose in this zone results in a corresponding increase in the free available chlorine.

II. MATERIALS AND METHODS

Break-point Chlorination is used for the removal of bound nitrogen from waster and more particularly controls the break-point chlorination reaction for removing ammonia from wastewater. It provides physical and chemical means for removing ammonia from waste water. Chlorine is added to the waste water until a point where Total Dissolves residual Chlorine has reached a minimum and NH_3-N disappears. The method involves addition of excess chlorine beyond the break-point chlorination to remove NH_3-N by forming different chloramines[6, 8].

2.1. Procedure

Initially we calculated the present percentage of activated chlorine in sodium hypochlorite by following procedure:
Take the sample and maintaining the pH around 3-4. Add 1 gm. of potassium iodide crystal in sample. Titrate with Sodium Thiosulphate until yellow color disappears. Add starch till blue color appears and then again titrate the sample with sodium thiosulphate until the blue color disappears. With the final reading from burette calculate the amount of chlorine present in sample [9].
After that prepare 1% solution of Sodium Hypochlorite. Use that 1% of solution for dosing different ppm (in the range of 0-110ppm) in 100ml waste water sample. After this 15 min residence time should be given and then calculate the amount of Free Residual Chlorine, which will help in finding the mount of chlorine required for the removal of Ammonical nitrogen from the waste water.

2.2. Advantages

- Low Cost
- High Reliability.
- Disinfection is not required.
- High Efficiency.

2.3. Limitations

- Large quantity of Cl^- required.
- NCl3 produced which is more harmful

III. RESULTS AND DISCUSSION

At 91 ppm, we found the Break Point Chlorination for the given waste water effluent of the Crude Refining industry. We also modified the method by changing the pH and temperature at the optimum dosage of the chlorine. Thus the optimum dose was found to be 91 ppm of 1% solution of sodium hypochlorite and the optimum conditions are 9 pH and 65^{o} C temperature. This shows the reduction of Ammonical Nitrogen from 38.32ppm to 7.12ppm.

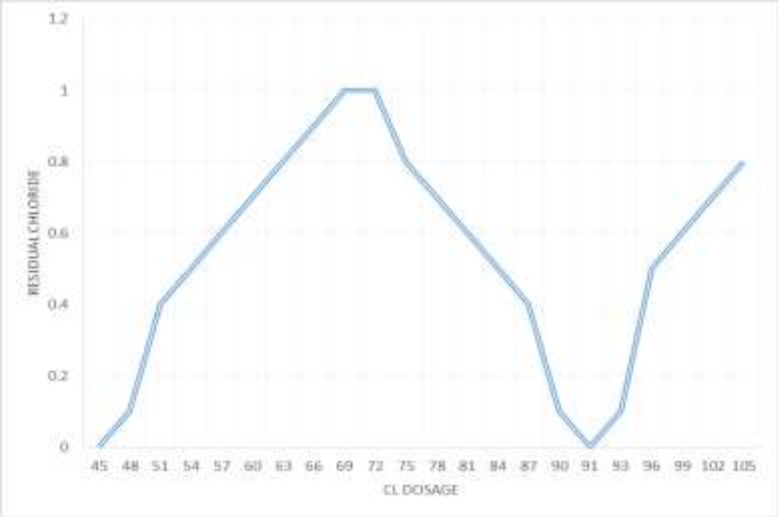

Figure 2.1: graph of obtainig break point chlorination.

Table 2.1: Final results of Ammonical nitrogen at different conditions.

Conditions	Ammonical nitrogen (ppm)
Initial	38.32
at 91ppm	22.08
at 91ppm with 9 pH	20.15
at 91ppm with 9pH at 65^{o} C	7.12

IV. CONCLUSIONS

From all the studies we have studied the various methods for the removal of the Ammonical Nitrogen from the waste water of the Crude Refining industry. Studying each method in detail its advantages and limitation and its features in detail we conclude that Break-point Chlorination method is the most effective considering the plant scenario in industry and its expenses and efficiencies.
Hence we experimented on the same method and have performed the analysis of the waste water effluent of the Crude Refining industry by using Break-point Chlorination method. Results which we gained are quite efficient as we got almost around 85% efficient removal of the Ammonical Nitrogen which would benefit the industry in meeting the statutory norms.

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