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Removal of Ammonical Nitrogen by Advance Oxidation

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Abstract — *Ammonical Nitrogen plays an important role for many industrial wastes as it may hamper the secondary biological system. It also produces many organic amines while reacting with them and plays a leading role for Eutrophication.. One of the chemical units at Ankleshwar GIDC has proposed to take up treatability studies involving various alternatives to reduce NH4-N in the secondary treated effluent of approximately 400 mg/l to less than 50 mg/l. Here in our study, we have classified techniques in to three categories named 1) chemical treatments 2) Physical Treatments and 3) Physico chemical Treatments. After thorough and extensive literature survey we have reached at conclusion that Electrochemical Oxidation is prominent method among many we would like to apply for removal of NH4-N on secondary outlet effluent. During overall treatability study we have applied two methods which are chemical addition (Precipitation) and Electrochemical Oxidation to the effluent and then we have compared the results of both methods and thus we concluded that by electrochemical oxidation we got reduction of NH4-N from 283 ppm to 3 ppm (99 %), Where as in chemical addition we have got reduction around 94 %.*

Keywords- *Ammonical Nitrogen, Eutrophication, Electrochemical Oxidation, Precipitation, Amines*

I. INTRODUCING AMMONICAL NITROGEN

Ammonical nitrogen is a measure for the amount of ammonia, a toxic pollutant often found in landfill leachates and in waste products, such as sewage, liquid manure and other liquid organic waste products. Large scale urbanization, a consequence of economic development is leading to production of huge quantities of waste water in India and posing serious environmental problems for their disposal. It is evident that the protection of our water resources is of major importance on a global scale. The treatment and disposal of sludge produced during waste treatment is one of the most critical environmental issues of today. Sludge produced is large in volume and hazardous. NH4-N has been identified as one of the major toxicants to microorganisms in the treatment system, suggesting that pre treatment prior to the biological treatment system is required to reduce the concentration of NH4-N. Ammonical Nitrogen contamination is highly toxic and it would adversely affect aquatic life if is discharged above sustainable limit. NH4-N is the toxicant that causes the death of tilapia fish. The high content of ammonical nitrogen is the major factor that affects the toxicity of wastewater.

II. LITRATURE SURVEY

A. Different methods for removal of Ammonical Nitrogen

Through extensive literature survey, we have identified few well defined processes for removal of Ammonical nitrogen at lab scale level.

Table-1

Chemical Processes for removal of NH_3-N	
1	MAP Process [1]
2	Reduction by Sodium Bi-Sulphate [3]
3	Reduction by Sodium Hypochlorite
Physical Process for removal of NH_3-N	
1	Reduction by Stripping Tower [4]
Chemical Oxidation Process	
1	Reduction by breakpoint chlorination
2	Reduction by Sodium Hypochlorite
Advanced Oxidation Process	
1	Reduction by electrochemical oxidation [5][6]

Note: The Sodium Hypochlorite process is a combination of chemical and electrochemical oxidation process.

B. Sampling for Treatability study:

At regular interval of one month time samples were taken for study purposes. Total five time sampling has carried out for different method's usage.

Table-2

Sr.No	Date of Sample Taken	Time of Sample taken	Quantity of sample taken	Initial Concentration of NH_3-N (Parts Per Million)
1	7/8/2014	10:30 am	20 Lit	416
2	8/9/2014	11:45 am	20 Lit	480
3	6/10/2014	16:20 pm	20 Lit	120
4	7/11/2014	15:37 pm	20 Lit	448
5	5/12/2014	16:28 pm	20 Lit	425

III. LABORATORY METHOD OF DETECTION OF NH_3-N

A. How to calculate quantum of Ammonical nitrogen.

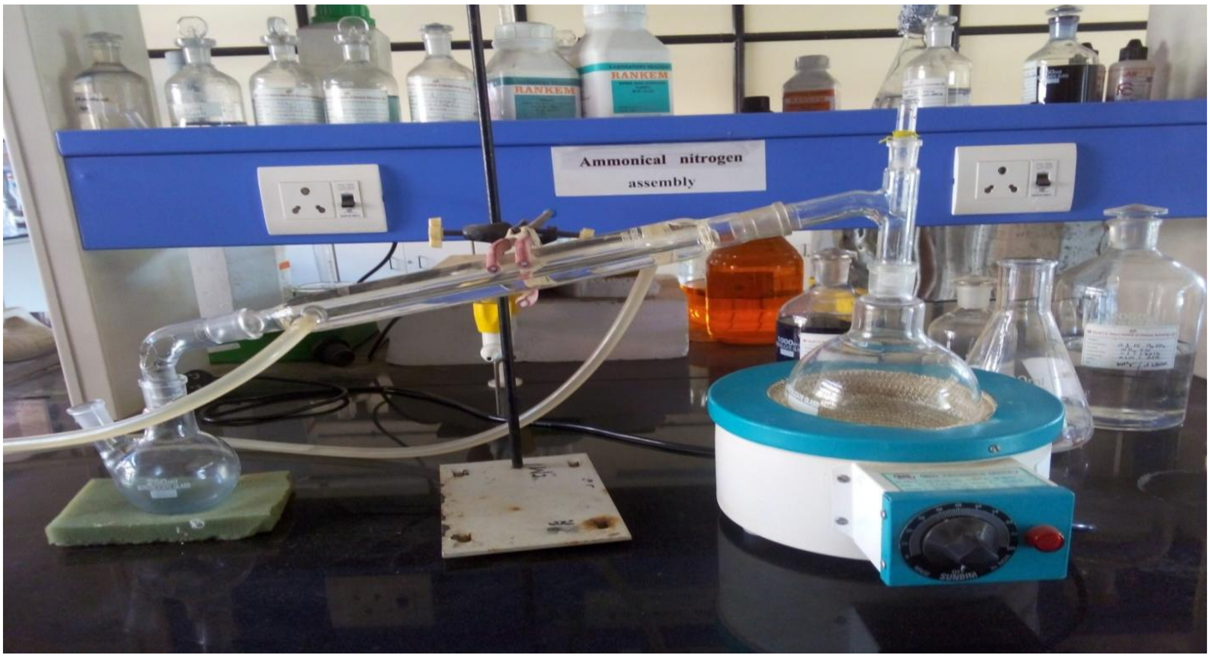


Figure-1

Distillation Process:

First set assembly as shown in the figure. Take 100 ml effluents in Round Bottom Flask. Heat it up to 90 to 100 ^{0}C for 1 hour. Collect distillate in receiver.

From the collected distillate (containing NH_4-N) take 25ml of distillate sample in conical flask.

Take 50ml of 2% Boric Acid and add in the flask. Then add 5 to 6 drop of Methyl Red as an indicator. Then Titrate it with 0.02N H_2SO_4Till color changes. Then take the reading for calculation of NH_4-N ppm calculations.

Ammonical Nitrogen (ppm) =

$$\frac{\text{Burette reading*N of } \quad \text{H2SO4*14000}}{\text{Volume of sample}}$$

(Ref: APHA 21th Edition, Standard Methods for examination of water & waste water, 2005 Centennial Edition. Section 4500-NH_3 C. page no. 4-110)

B. Electrochemical Oxidation Process for Removal of NH_3-N :

- Voltage taken was 1.86 volt at a 5amp current.

Table-2

Sr .No	Current AMP	Voltage Volt	Time (hr)	Concentration	% Removal
1	5.00	1.86	0	296	0.0
2	4.96	1.85	1	281	5
3	4.91	1.88	2	268	10
4	4.91	1.92	3	242	18
5	4.92	1.94	4	204	31

Here in our first run of the setup, we have got reduction from 296 ppm to 204 ppm (31 %).

- Voltage taken was 1.96 volt at a 5amp current

Table-3

Sr .No	Current AMP	Voltage Volt	Time (hr)	Concentration	% Removal
1	4.99	1.96	1	299	0.0
2	4.96	1.98	2	279	7
3	4.95	1.96	3	259	13
4	4.91	1.97	4	235	21
5	4.92	1.95	5	197	33

Here in our second run of the set up we have got reduction from 299 mg/l to 197 mg/l (33 %).

- Voltage taken was 1.82 volt at a 5amp current

Table-4

Sr .No	Current AMP	Voltage Volt	Time (hr)	Concentration	% Removal
1	4.92	1.82	1	313.6	0.0
2	4.90	1.88	2	285	9.12
3	4.87	1.91	3	243	22.51
4	4.86	1.93	4	221	29.53
5	4.86	1.94	5	197	37.18

Here in our third run of the set up we have got reduction from 313 mg/l to 197 mg/l (37 %).

- Voltage taken was 4.83 volt at a 10amp current

Table-5

Sr .No	Current AMP	Voltage Volt	Time (hr)	Concentration in (ppm)	% Removal
1	10	4.83	11:30 am	283	0.0
2	9.96	4.72	11:00am	280.2	1.0
3	9.95	4.68	11:30am	252	10.6
4	9.93	4.50	12:00 am	193.2	31.73
5	9.93	4.64	12:30 pm	168	40.63
6	9.92	4.74	13:00 pm	131.6	53.49
7	9.93	4.80	13.30 pm	126	55.47
8	9.91	4.83	14:00 pm	86	69.61
9	9.90	4.85	14.30 pm	14	95.05
10	9.90	4.87	14.40 pm	11.2	96.04
11	9.90	4.87	14.50 pm	8.6	96.9
12	9.90	4.87	15:00 pm	5.6	98.02
13	9.90	4.87	15.10 pm	2.8	99.01

IV. CHEMICAL PROCESS OF REMOVAL OF AMMONICAL NITROGEN

A. From several chemical processes for removal of NH_4-N it has been derived that MAP (Magnasium Ammonium Phosphate) is most promising one.
As per mentioned above after primary analysis, for final treatability study MAP process has choose.

Table-6

Sr .No	Date of Sampling	Initial (ppm)	Final (ppm)	Percentage Removal (%)	pH
1	7/8/2014	296.8	100.8	66	7-8
2	8/9/2014	299.6	113.6	62	7-8
3	6/10/2014	313.6	16.8	94	8-9
4	7/11/2014	283	22.4	92	8-9
5	5/12/2014	296	23	92.22	8-9

Percentage Reduction of NH_4-N by MAP (MgCl2) is 92 % maximum.

Table-7

Sr .No	Date of Sampling	Initial (ppm)	Final (ppm)	Percentage Removal (%)	pH
1	7/8/2014	296.8	127.3	57	7-8
2	8/9/2014	299.6	143.5	52	7-8
3	6/10/2014	313.6	106.4	66	8-9
4	7/11/2014	283	104.7	63	8-9
5	5/12/2014	296	102	65	8-9

Percentage Reduction of NH_4-N by MAP (MgO) is on an average 65%

V. COMPARATIVE STUDY OF RESULT

A. Comparison graph of all methods in percentage reduction:

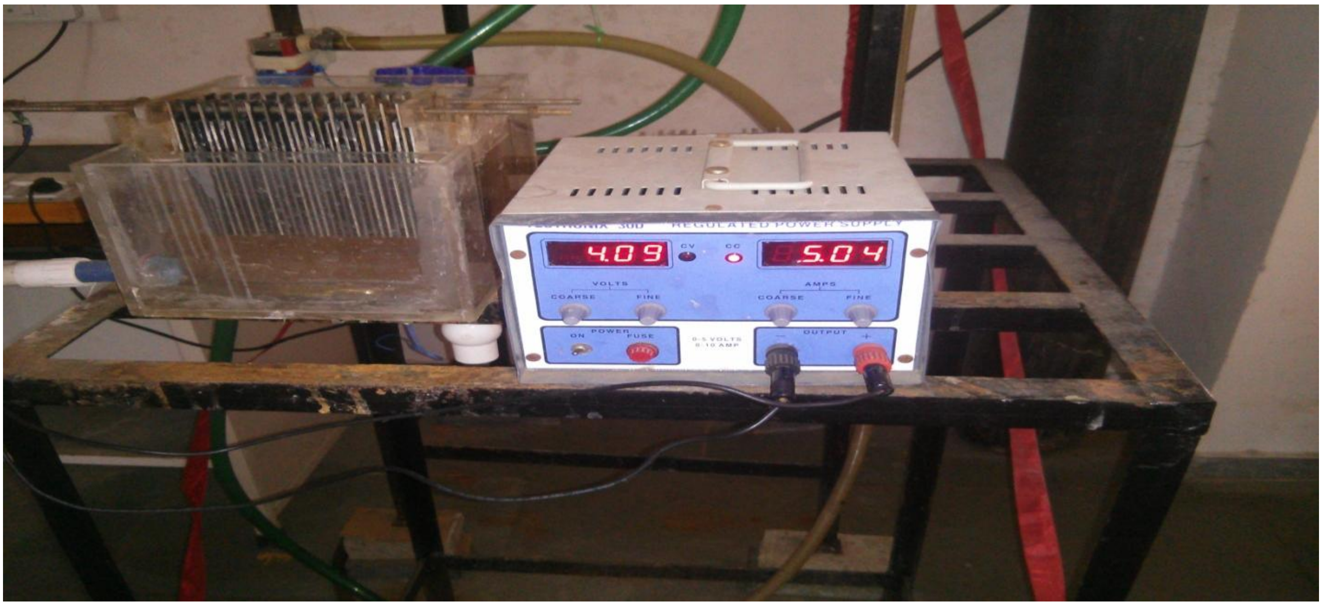
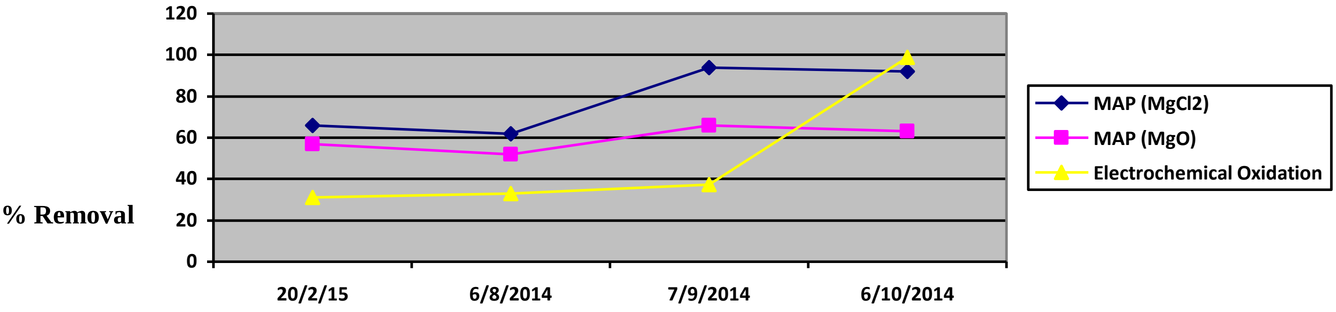


Figure-2: Electochemical Oxidation Lab Scale Unit



Graph-1 : Comparison of % removal by all three processes

The graph indicate that for more than 5 hours of electrochemical oxidation gives more batter result in compare to it’s competitor MAP process.

B. Running Cost

The cost of running also plays an important role for selecting any new technology, hence the running and energy cost of electrochemical oxidation is depicted by following method.The average current efficiency (ACE) and energy consumption (EC) were determined using Equations after considering the removal of NH_3-N :

EC = $(\Delta Ec \times I \times t)/(3600 \times V)$ kWh. L^{-1} = 4.87*9.90*4/ (3600*4) = 0.01333 kWh. L^{-1}

Where, **t** (s) = time of the electrochemical treatment, **ΔEc** (V) = average cell voltage,
I (A) = electrochemical treatment current and **V** (L) = sample volume;

Now here for 10000 liter of effluent we required: 0.01333 * 10000 = **133.3 kWh**.

As per electricity rate (5 rupees per unit) for treatment of 10000 liter of effluent, we required: **133.3 * 5 = 666.5** Rs.

VI. CONCLUSION

As a treatment which is electrochemical oxidation process reduces 283 ppm to 2.8 ppm is 99.01 % removal at 9.90 Amp and 4.87 volt.

Initial pH range from 7 and 9 was favorable for electrochemical ammonia oxidation.

1) Changes in colour were significant and resulted in colourless solutions for some samples, even when minimal change in COD was observed.
2) It does not produce any kind of sludge.
3) The ammonia oxidation rates with Cu/Zn cathode were higher than that with Ti and Fe cathode. The nitrate formed during electrolysis with Cu/Zn was the lowest than that with other cathodes. The reason why the nitrate-N concentration was the lowest with Cu/Zn cathode was that because of its high reduction ability.

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