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Microbial Degradation of Urea from Urea Bearing Wastewaters

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Abstract

Urea and ammonia are mostly present in wastewaters from nitrogenous fertilizer industries. Urea can not be oxidized by usual oxidation methods, microbiological hydrolysis of urea is necessary for removal of urea from wastewater. Biological degradation of urea is a two staged process; (i) urea hydrolysis and (ii) ammonia stripping/nitrification-denitrification. Microbiological hydrolysis of urea through biohydrolyzer removes urea from fertilizer effluents , in which ,ureolytic bacteria Bacillus Pasteurii converts urea into ammonia and carbon dioxide through ammonium carbonate as an intermediate product. Removal of ammonia is either by stripping or converting into nitrate on nitrification by chemoautotraphic bacteria Nitrosomonas sp. and further by Nitrobacter sp. into nitrate. On dentirification , nitrate is finally converted into nitrogen gas by means of heterotrophic bacteria. Based on earlier laboratory investigations, urea bio-hydrolyser was designed, installed and commissioned in fertilizer industry as additional full scale unit to treat urea and ammonia bearing wastewaters. Ammonia stripped effluent was mixed with septic tank effluents from industry and township sewage and routed through various lagoons cultured with algae – chlorella to minimize nitrogen. Evaluation of full scale urea bio-hydrolyser and effluent treatment plant before and after modifications at ETP is discussed in this paper.

Key Words: Urea, ammonia, nitrogenous fertilizer industry, microbiological treatment, nitrification, urea bio-hydrolysis

Introduction

In India, per hectare consumption of fertilizer nutrients has been steadily increasing frommearly 0.55 kg in 1950-51 to 68.00 kg in 1995. The production capacity of nitrogenous fertilizer in the country has boost up from a modest capacity of 85,000 tonnes in 1950-51 to 9.480 million tones in March, 1997. The projected production by the end of 2004-05 is 9.940 million tonnes (India 1995 and Monthly Review of Indian Economy 1997). Coal based nitrogenous fertilizer industries in India produced mostly ammonia, urea, nitric acid, ammonium nitrate and ammonium bicarbonate using coal and fuel oil as raw materials. Coal is converted into carbon- dioxide. Ammonia is manufactured from atmospheric nitrogen (air) and steam. Urea and ammonium bicarbonate are manufactured from carbon dioxide and ammonia. Ammonium nitrate is synthesized from nitric acid and ammonia. Therefore, the wastewater from fertilizer industry contains nitrogenous compounds viz, urea, ammonia, nitrate and ammonium bicarbonate. Urea and ammonia are the major constituents of wastewater from nitrogenous fertilizer industry manufacturing ammonia and urea as the major products. The volume of wastewater from ammonia production generally varies from 4.9 to 6.7 m^3 /tonne of ammonia produced with concentrations of ammonia and urea varying from 4.65 to 10.0 and 15.0 to 17.5 kg/tonne of ammonia produced, respectively. Wastewater generation from urea plant varies from 8.0 to 12.0 m^3 tonne of urea produced depending on the quantity of raw materials consumption. Ammonia and urea concentrations varying between 200 –1500 mg/L and 340-20,000 mg/L, respectively (IS-9841 1981).

Urea as such is non-toxic for human, animal and aquatic life even at high concentrations. The test fish – Creek Chub in the Detroit river were observed to survive even at higher dose of more than 1000 mg/L of urea (Gillette*et al* 1952). However, urea under favorable conditions hydrolyses to ammonia and carbondi-oxide. An ammonia concentration of 1.2 to 3.0 mg/L is toxic to fish.

Evans *et al.* 1973 reported that 4 to 6 days are required for urea degradation and 20^0c with urea concentrations ranged between 1 to 15 mg/L and 14 days or more at a temperature lower than 8^0c. This indicates that urea hydrolysis is a very slow process and can take place only in presence ofurase, otherwise the hydrolysis may assume to be negligible.

Process of Nitrogen Removal

Nitrogen removal through microbiological treatment of wastewater containing urea involves the following unit processes:

Urea Hydrolysis

Urea hydrolysis is brought out by microorganisms mainly ureolytic bacteria Bacillus pasteurii as follows:

$$O{=}C\begin{matrix} NH_2 \\ NH_2 \end{matrix} + H_2O \longrightarrow (NH_4)_2\,CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O$$

Urea	Water	Ammonium Carbonate	Ammonia	Carbon-dioxide	Water

Ammonia and ammonium ions in aqueous solution remain in equilibrium as follows:

$$NH_4 \longleftrightarrow NH_3 + H^+$$

At pH 7.0 and temperature 0 to 250 °C, over 99% of ammonical nitrogen is in ammonium (NH_4^+) form. Autotrophs include the nitrifying bacteria which obtain energy from oxidizing inorganic nitrogen (chemoautotroph) and algae which obtain energy from sunlight (photoautotroph).

Nitrification

Ammonia is biologically oxidized to nitrate in a two stage process by two groups of chemoautotrophic bacteria which operates in sequence. The first step is oxidizing ammonia into nitrite by members of genus *Nitrosomonas sp*. Nitrite is further oxidized to nitrate by members of genus *Nitrobacter sp.* as follows:

$$2NH_4^{\ +} + 3O_2 \xrightarrow{\text{Nitrosomonas Sp.}} 2\,NO_2 + 4\,H^+ + 2H_2O + \text{Energy}$$

$$2NO_2 + O_2 \xrightarrow{\text{Nitrobacter Sp.}} 2NO_3 + \text{Energy}$$

Energy released in this oxidation is used in synthesizing cell materials from carbon-di-oxide. It is evident from these equations that oxygen is required for nitrification process which gives rise to oxygen demand in wastewater. Liberation of hydrogen ion may result in pH drop in poorly buffered wastewater, resulting in loss of process stability.

Denitrification

Denitrification of nitrate is brought out by heterotrophic bacteria first into nitrite and then to nitrogen gas. As the energy yield is lower than that from oxygen respiration, denitrification is effective only at low dissolved oxygen concentrations. An external carbon source is necessary to obtain maximum reaction rate. Methanol can be used as one of the carbon source and the reaction can be represented as follows:

$$NO_3 + CH_3OH \longrightarrow N_2 + CO_2 + H_2O + OH^-$$

Urea biohydrolyser breaks urea molecule into ammonia and carbon-di-oxide with the help of ureolytic bacteria *Bacillus pasteurii*. After hydrolysis the ammonia produced is stripped off. The remaining ammonia nitrogen undergoes nitrification producing nitrate. Nitrate and ammonia are utilized by algae for growth. Unutilized nitrate is converted into nitrogen gas after denitrification. Thus nitrogen free effluent is produced.

Brief details of Nitrogenous Fertilizer Industry under Study

The major products being produced at the coal based nitrogenous fertilizer Industry are ammonia, Urea, nitric acid, ammonium nitrate, ammonium bicarbonate, coke and tar. The rated capacities of these products are 900, 1000, 200, 35, 12, 325 and 10 tonnes/ d, respectively.

Total water requirement of the fertilizer Industry was around 79124 m^3/d. This includes water for process, cooling and domestic uses. Wastewater generations from the various unit processes of the industry were monitored. The total wastewater generation observed to be in the range of 34608 – 37944 m^3/d. Table 1 presents the quantity of wastewater generated from the various process units of the fertilizer industry.

This paper gives an account of studies on a full scale urea bio-hydrolizer cum stripper as additional unit and effluent treatment plant to treat nitrogenous wastewater from fertilizer industry.

Materials and Methods

Effluent treatment plant

Nitrogenous fertilizer industry under study had full scale effluent treatment plant comprising of ten lagoons/ponds of various capacity of 100000 m^3. Total detention time of all ten lagoons at ETP was 25 days. As lagoons 1, 2, 3 were under repairs, wastewater from urea manufacturing plant was directly received in lagoon No.4. Septic tank effluents from the industry and township sewage were also being discharged in this lagoon and the mixed effluents were routed through various lagoons for further treatment. Treated urea effluent was discharged into lagoon No.9. Other combined wastewater from coke oven, ammonium bicarbonate, nitric acid and resorcinol plants was received in lagoon No.9. Effluent from steam generation was directly discharged into treated effluent from lagoon No. 9, into natural drain, which further joins a river after traveling a distance of about 500 meters.

Table 1. Quantity of wastewater generated from various process units

Sr. No.	Process Unit	Quantity, m^3/day Range	Average
1.	Oil Gasification	1656 - 752	1680
2.	Rectisol	792 - 936	840
3.	DM		
	-Acidic	1344-1560	1440
	-Alkaline	864 - 1056	984
4.	Steam Generation	1584 -1656	1608
5.	Compressor House	384 -528	456
6.	Coal and handling house	384 -576	480
7.	Urea	1800 -1968	1896
8.	Coke Oven	1152 -1296	1224
9.	Nitric Acid	360 - 528	432
10.	Ammonium Nitrate	288 - 432	360
11.	Ammonium Bi-carbonate	168 - 264	216
12.	Power Plant	9600 -10800	10128
13.	Septic Tank Effluent	14322 -14592	14424
14.	Combined Effluent	34608 -37944	36168

Performance evaluation of ETP was carried out for 7 days. Wastewater samples at various stages of treatment (lagoons) at ETP were collected over a period of 8 hours. These samples were analyzed for pH, TDS, SS, total and free ammonical nitrogen, total kjeldahl nitrogen, nitrite and nitrate nitrogen as per Standard Methods 1989. Urea was analysed as per procedure described Watt and Chrisp 1954. Characteristics of influent and effluent from various lagoons at ETP are presented in Table 2.

Treated effluent from ETP does not confirm to the standards prescribed by the MEF/State pollution Control Board for discharge of effluent into Inland Surface Water with respect to parameters- total ammonia nitrogen, free ammonia nitrogen, total kjeldahl nitrogen and nitrate nitrogen.

Based on performance evaluation of ETP and bench scale laboratory studies on urea bio-hydrolyser conducted earlier, modifications at ETP were suggested to remove urea and ammonia from urea bearing wastewater. Urea bio-hydrolyser cum stripper was designed and its installation as an additional unit before lagoon no. 1 at ETP was recommended.

Modified Effluent Treatment Plant- Full Scale Urea Bio-hydrolyser

Modified effluent treatment plant comprises a full scale urea bi-hydrolyser unit followed by ten lagoons in series. Urea bio–hydrolyser plant was installed and commissioned. The plant comprises of 16 compartments of different sizes arranged in 8 horizontal rows. Total volume of all these compartments was 6012 m^3 with detention period of 90 hours. The layout plan of urea bio-hydrolyser is shown in Fig.1. Pressurized steam was introduced at the bottom of compartment Nos. 11, 12,13,14,15 and 16 to facilitate ammonia stripping, produced during urea hydrolysis. In addition, ammonia from hydrolyser plant was further stripped off through cascade aeration system. Further, ammonia stripped effluent was then routed through lagoons 1 to 8A to reduce ammonia from the effluent. Septic tank effluent from industry and township was being discharged into lagoon 4 to remove ammonia from wastewater. Intermittent addition of algae- chlorella in lagoons was practiced.

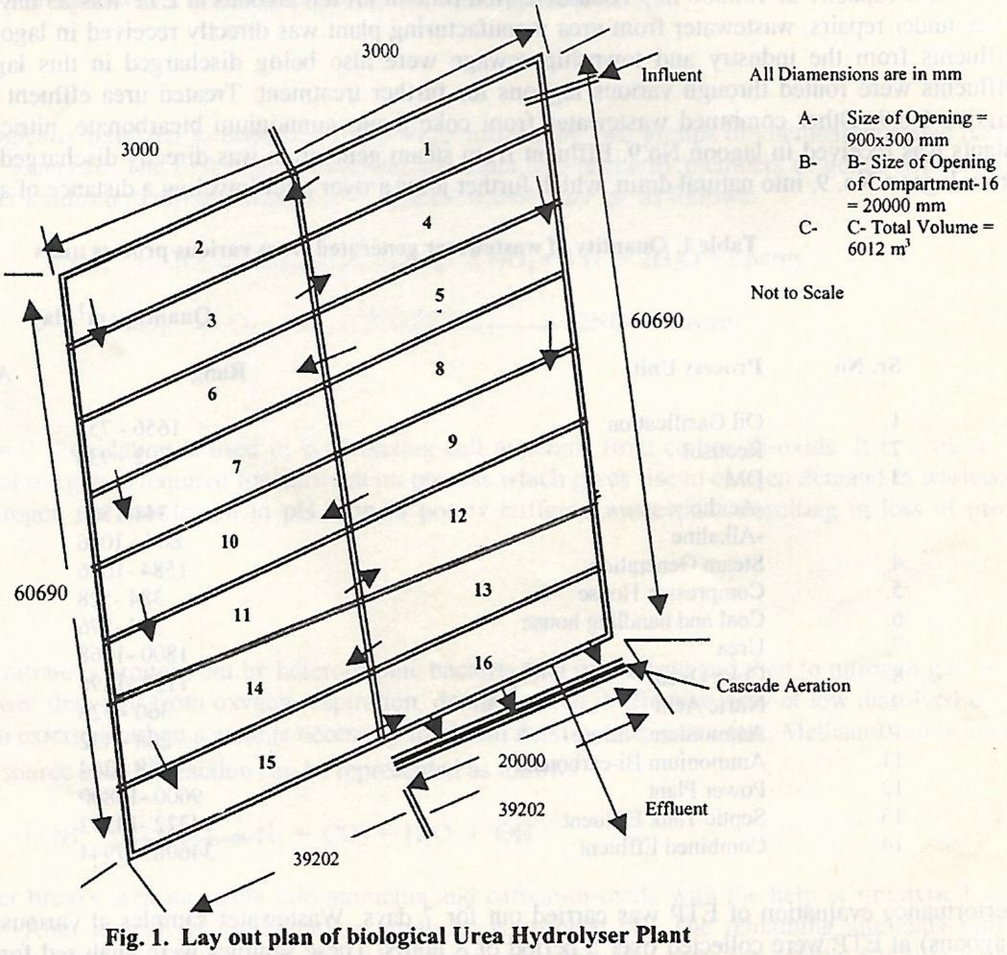


Fig. 1. Lay out plan of biological Urea Hydrolyser Plant

Table 2. Characteristics of influent and effluent from various lagoons at ETP

Effluent Type	Parameters														
	pH	TDS	SS	DO	COD	BOD	Total ammonical nitrogen	Free ammonical nitrogen	Total Kjeldahl nitrogen	Urea	Nitrite	Nitrate	Oil & grease	Total chromium (Cr)	Cyanide (Cn)
Effluent from urea plant to lagoon 4	9.0 ± 0.6	668 ± 82	22 ± 7	1.8 ±0.2	1.42 ±26	60 ±15	1810 ±94	722 ±88	2440 ±146	1350 ±70	3 ±2	36 ±8	32 ±6	ND	ND
Lagoon 4 effluent	9.0 ±0.5	792 ±98	7 ±3	2.2 ±0.3	88 ±16	35 ±8	665 ±50	348 ±24	1142 ±74	936 ±56	6 ±3	34 ±6	26 ±5	ND	ND
Lagoon 5 effluent	8.6 ±0.4	786 ±86	5 ±2	2.5 ±0.4	52 ±10	20 ±5	612 ±62	264 ±21	1030 ±44	856 ±28	8 ±3	30 ±8	19 ±6	ND	ND
Lagoon 6 effluent	8.6 ±0.4	770 ±80	4 ±2	3 ±1	44 ±8	15 ±3	577 ±78	126 ±13	958 ±38	750 ±32	9 ±2	32 ±6	16 ±4	ND	ND
Lagoon 7 effluent	8.5 ±0.4	764 ±82	3 ±1	3.2 ±0.4	36 ±5	12 ±3	530 ±46	84 ±8	764 ±52	532 ±40	10 ±2	31 ±4	10 ±2	ND	ND
Lagoon 8 effluent	8.4 ±0.4	752 ±83	3 ±1	3.5 ±0.4	30 ±6	8 ±2	494 ±46	48 ±10	615 ±44	366 ±28	11 ±2	30 ±4	10 ±2	ND	ND
Lagoon 8A effluent	8.3 ±0.5	728 ±88	3 ±1	3.9 ±0.4	24 ±4	6 ±2	348 ±28	30 ±6	424 ±68	274 ±46	12 ±8	26 ±3	9 ±2	ND	ND
Factory combined effluent at lagoon 9	8.4 ±0.6	918 ±108	163 ±23	2.0 ±0.4	252 ±28	120 ±30	105 ±26	54 ±22	160 ±40	12 ±4	20 ±8	42 ±10	14 ±4	ND	ND
Lagoon 9 effluent	8.3 ±0.4	848 ±84	22 ±9	4.0 ±0.3	35 ±8	10 ±4	202 ±22	26 ±6	282 ±42	84 ±8	14 ±4	22 ±4	6 ±2	ND	ND

All values except pH are in mg/L, ND- Not detectable

Table 3. Characteristics of influent and effluent from each compartment of urea biohydroliser plant

Effluent Type	Parameters									
	Temperature	pH	TDS	SS	Total ammonical nitrogen	Free ammonical nitrogen	Total Kjeldhal nitrogen	Urea	Nitrate nitrogen	Nitrite nitrogen
Compartment No. 1 influent	24 ±3	10.1 ±0.3	1726 ± 120	126 ±18	975 ±55	794 ±106	1840 ±168	1230 ±182	0.9 ±0.1	2.0 ±1.0
Compartment No. 1 effluent	25 ±3	10.1 ±0.3	1694 ±104	794 ±76	984 ±64	804 ±101	1794 ±152	1200 ±176	1.28 ±0.10	2.1 ±1.1
Compartment No. 2 effluent	25 ±3	10.1 ±0.3	1538 ±102	748 ±84	996 ±58	864 ±94	1678 ±152	1200 ±176	1.28 ±0.11	2.2 ±1.1
Compartment No. 3 effluent	25 ±3	10.1 ±0.3	1420 ± 96	680 ±92	1034 ±68	936 ±88	1476 ±136	854 ±122	1.36 ±0.11	2.3 ±1.1
Compartment No. 4 effluent	25 ±2	10.2 ±0.2	1392 ±90	656 ±74	1082 ±78	996 ±92	1282 ±140	628 ±108	1.40 ±0.14	2.4 ±1.2
Compartment No. 5 effluent	25 ±2	10.2 ±0.2	1356 ±92	632 ±68	1132 ±80	1074 ±86	1204 ±132	440 ±82	1.46 ±0.12	2.5 ±1.2
Compartment No. 6 effluent	25 ±2	10.3 ±0.2	1318 ±91	600 ±52	1158 ±84	1092 ±90	1196 ±124	356 ±64	1.52 ±0.10	2.6 ±1.2
Compartment No. 7 effluent	25 ±2	10.3 ±0.2	1250 ±66	580 ±48	1004 ±92	978 ±84	1042 ±116	334 ±58	1.64 ±0.11	2.7 ±1.1
Compartment No. 8 effluent	25 ±2	10.3 ±0.2	1222 ±78	528 ±50	820 ±68	798 ±70	886 ±110	310 ±50	1.76 ±0.13	2.7 ±1.2
Compartment No. 9 effluent	25 ±3	10.2 ±0.2	1204 ±62	462 ±38	806 ±52	728 ±46	865 ±112	294 ±56	1.88 ±0.12	2.8 ±1.2
Compartment No. 10 effluent	25 ±3	10.2 ±0.2	1178 ±72	370 ±42	712 ±46	641 ±48	830 ±98	278 ±52	2.06 ±0.14	2.9 ±1.1
Compartment No. 11 effluent	25 ±3	10.1 ±0.2	1144 ±64	296 ±38	604 ±50	558 ±42	782 ±84	264 ±64	2.18 ±0.18	3.0 ±1.1
Compartment No. 12 effluent	25 ±3	10.1 ±0.2	1109 ±70	252 ±32	534 ±38	496 ±44	622 ±76	238 ±56	2.26 ±0.20	3.2 ±1.1
Compartment No. 13 effluent	24 ±3	10.0 ±0.2	1090 ±62	224 ±36	478 ±32	442 ±40	572 ±64	222 ±60	2.56 ±0.24	3.5 ±1.2
Compartment No. 14 effluent	24 ±3	10.0 ±0.2	1058 ±74	208 ±32	414 ±30	394 ±42	500 ±58	196 ±70	2.64 ±0.26	3.7 ±1.2
Compartment No. 15 effluent	24 ±3	10.0 ±0.2	1028 ±68	196 ±24	382 ±34	346 ±36	442 ±56	178 ±62	2.66 ±0.28	3.8 ±1.2
Compartment No. 16 effluent	24 ±3	10.0 ±0.2	994 ±60	138 ±16	346 ±32	304 ±32	400 ±52	160 ±52	2.70 ±0.30	4.0 ±1.2

All values except pH are in mg/L, ND- Not detectable

Microbial culture produced during earlier bench scale study was used for start up of urea bio-hydrolyser. Chalked paddy straw of 10 to 50 mm size was used as the carbon source for microorganisms. As urea bearing wastewater was Phosphate deficient, Super phosphate was added in requisite doses to supplement phosphate nutrient to microorganisms.

The performance of the Urea bio-hydrolyser unit and modified effluent treatment plant were monitored. Hourly wastewater samples were collected from each compartment of the urea bio-hydrolyser over a period of 8 hours for 7 days. The samples were analyzed for pH, TDS, SS, Total ammonical Nitrogen, Free ammonical Nitrogen, Total Kjeldahl Nitrogen, Nitrite Nitrogen, Nitrate Nitrogen and urea. Characteristics of influent and effluent from each compartment of urea bio-hydroliser plant are presented in Table 3. Hourly samples from each lagoon were also collected over a period of 8 hours for 7 days and analyzed for afore-referred parameters. Characteristics of effluent and influent from urea bio-hydroliser and effluent characteristics from various lagoons at modified effluent treatment plant are in Table 4. The characteristics of combined final treated effluent from the fertilizer industry being discharged into river are presented in Table 5.

Table 4. Characteristics of influent and effluent from urea-bio-hydrolyser plant and various lagoons of ETP

Effluent Type	Parameters														
	pH	TDS	SS	DO	COD	BOD	Total ammoniical nitrogen	Free ammonical nitrogen	Total Kjeldahl nitrogen	Urea	Nitrite	Nitrate	Oil & grease	Total chromium (Cr)	Cyanide (Cn)
Urea bio-hydrolyser influent	10.1 ±0.3	1726 ±120	126 ±18	ND	332 ±56	200 ±25	975 ±55	794 ±106	1840 ±168	1230 ±182	0.90 ±0.10	2 ±1	45 ±10	ND	ND
Urea bio-hydrolyser effluent	10.0 ±0.2	994 ±60	138 ±16	0.5 ±0.1	258 ±48	145 ±20	346 ±16	304 ±32	400 ±52	160 ±52	2.70 ±0.30	4 ±1	40 ±8	ND	ND
Lagoon 1 effluent	9.9 ±0.2	750 ±22	100 ±8	0.6 ±0.2	216 ±32	105 ±16	316 ±20	282 ±30	382 ±48	142 ±46	4.00 ±0.80	4.0 ±1.0	34 ±9	ND	ND
Lagoon 2 effluent	9.7 ±0.3	700 ±24	74 ±6	1.1 ±0.2	186 ±36	85 ±20	288 ±22	264 ±28	367 ±44	104 ±32	6.90 ±0.60	5 ±1	32 ±8	ND	ND
Lagoon 3 effluent	9.6 ±0.3	644 ±16	53 ±7	1.3 ±0.3	158 ±24	58 ±13	256 ±28	240 ±24	350 ±38	56 ±16	6.80 ±0.70	5 ±1	30 ±7	ND	ND
Lagoon 4 effluent	9.6 ±0.4	604 ±20	35 ±4	2.0 ±4	102 ±12	32 ±6	234 ±24	212 ±22	371 ±34	32 ±8	8.15 ±0.85	5 ±1	25 ±5	ND	ND
Lagoon 5 effluent	9.6 ±0.3	584 ±16	25 ±3	2.5 ±0.4	62 ±10	28 ±4	208 ±22	194 ±20	320 ±30	20 ±6	9.35 ±0.85	6 ±1	19 ±3	ND	ND
Lagoon 6 effluent	9.5 ±0.4	542 ±14	17 ±3	3.1 ±0.3	50 ±7	20 ±2	184 ±20	160 ±16	250 ±26	12 ±5	11.50 ±0.5	7 ±2	15 ±2	ND	ND
Lagoon 7 effluent	9.5 ±0.3	504 ±10	10 ±2	3.6 ±0.3	38 ±5	15 ±2	162 ±22	124 ±25	198 ±25	8 ±4	12.20 ±0.9	9 ±2	11 ±2	ND	ND
Lagoon 8 effluent	9.4 ±0.3	480 ±12	7 ±2	4.0 ±0.3	34 ±6	11 ±3	138 ±20	82 ±18	132 ±24	5 ±2	14.00 ±1.0	10 ±3	7 ±2	ND	ND
Lagoon 8A effluent	9.0 ±0.3	462 ±18	5 ±2	4.9 ±0.2	30 ±5	7 ±2	112 ±20	60 ±16	108 ±20	2 ±1	16.75 ±0.75	12 ±3	5 ±1	ND	ND
Factory combined effluent to lagoon 9	7.6 ±0.7	952 +96	140 ±8	1.9 ±0.2	284 ±54	130 ±18	85 ±16	42 ±12	88 ±16	1 ±1	8.95 ±0.95	45 ±8	13 ±2	0.07 ±0.02	0.10 ±0.03
Lagoon 9 effluent	8.1 ±0.2	946 ±84	36 ±6	4.7 ±0.3	42 ±8	14 ±4	76 ±6	7 ±2	52 ±12	ND	13.10 ±2.00	15 ±1	7 ±0.01	ND	0.03 ±0.03

All values except pH are in mg/L, ND- Not detectable

Results and Discussions

Initial urea concentrations, 1350 ± 70 mg/L from urea bearing wastewater was reduced to 274± 46 mg/L during wastewater treatment in lagoons 4 to 8 A. Biological nitrification resulted in increase of nitrite nitrogen concentrations in effluent from lagoons. Similarly, reduction in concentration of nitrate nitrogen in effluent from lagoons indicating occurrence of denitrification process in various lagoons. High concentration of total ammonical nitrogen even after its utilization by algae in lagoons may be due to biological hydrolysis of urea in presence of sewage.

After modifications at ETP, urea by hydrolyser reduces initial concentration of urea, 1230± 180 mg/L from urea bearing waste water to substantially low concentrations, 160 ± 52 mg/L, thereby achieving 85 to 90 % urea hydrolysis. The treated effluent from urea bio-hydrolyser contained free ammonia nitrogen ranging between 272 to 336 mg/L, removing around 61.3 to 62.9% of free ammonia by ammonia stripping. Lagoon 1 received low concentrations of urea (160 $\pm$ 52 mg/L) total Kjeldahl nitrogen (400 $\pm$52 mg/L)

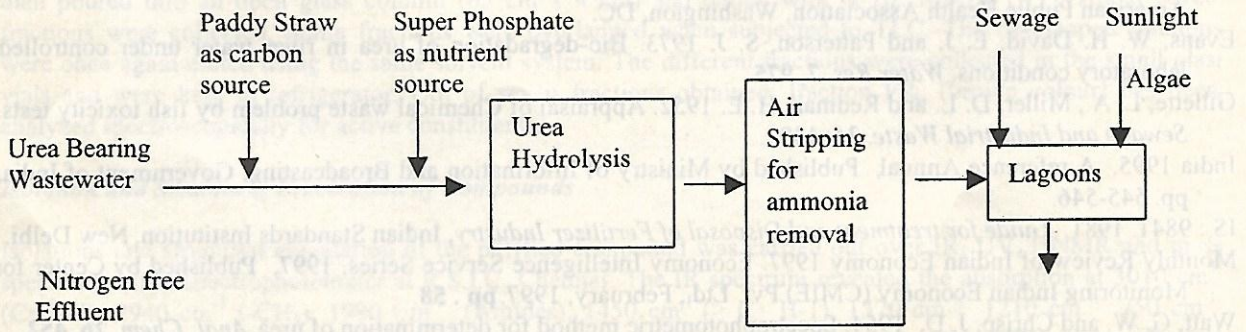
Table 5. Characteristics of combined treated effluent discharged in to River

Sr. No.	Parameter	ETP combined treated effluent	Standard for treated effluent (Inland surface water) MoEF*	SPCB#
1.	pH	7.5 – 8.0	5.5 – 9.0	6.5 – 8.0
2.	Total dissolved solids (TDS)	750 $\pm$52		
3.	Suspended Solids	46 $\pm$14	100	100
4.	Dissolved Oxygen Demand (DO)	4.8 – 5.2	-	-
5.	Chemical Oxygen Demand (COD)	54 $\pm$18	250	250
6.	Biochemical Oxygen Demand (BOD, d, 20 °C)	16.5 $\pm$5	30	30
7.	Total Ammonical Nitrogen	40 $\pm$5	50	75
8.	Free Ammonical Nitrogen	2.3 $\pm$0.3	5	4
9.	Total Kjeldahl Nitrogen	52 $\pm$12	100	100
10.	Nitrite (NO_2) Nitrogen	7.2 $\pm$0.4	-	-
11.	Nitrate (NO_3) Nitrogen	9.0 $\pm$0.8	10	10
12.	Urea	ND	-	-
13.	Total Phosphate	0.08 $\pm$0.3	5	-
14.	Total Phenolics	0.3 $\pm$0.1	1	-
15.	Cyanides	0.02 $\pm$0.01	0.2	-
16.	Fluorides	ND	2.0	-
17.	Oil and grease	4.6 $\pm$2.1	10	10
18.	Heavy Metals			
	- Iron (Fe)	0.52 +0.08	3	3
	- Lead (Pb)	0.002 +0.001	1	1
	- Zinc (Zn)	0.11 +0.04	5	5
	- Nickel (Ni)	ND	3	3
	- Chromium	ND	2	2

All values except pH are in mg/L, ND- Not detectable, * Ministry of Environment and Forests, Govt. of India, # State Pollution Control Board

And total ammonia nitrogen (346 $\pm$32 mg/L) for further treatment as compared to concentrations before modifications at ETP.

The urea bio-hydroliser unit was designed to accept initial urea concentrations up to 6000 mg/L tohydrolyse 90 to 95% urea from urea bearing wastewater. The flow sheet of urea bio-hydroliser and removal of nitrogen from the wastewater is as follows-



Paddy straw served as carbon source to Uerolytic bacteria *Bacillus pasteurii* and algae utilized ammonia nitrogen for their growth. Urea is being hydrolised into ammonia which then stripped off at high pH and also by injecting steam. Up to compartment no. 6 a constant increase in ammonia concentrations and constant decrease in urea concentrations indicating brisk reaction of urea hydrolysis. Resulting in 70 to 73% was removal in first 30 hours. Remaining 15 to 17% urea was removed in the remaining 10 compartments of urea bio-hydrolyser plant. However, the concentrations of ammonia in these compartments showed lower values as compared tostricometric values, due to ammonia stripping at high pH of wastewater. At pH above 8.6, ammonia is released from ammonia solution in to the atmosphere. Thus, by maintaining high pH, ammonia stripping was achieved. Ureabiohydroliser removed about 61 to 63% ammonia nitrogen due to ammonia stripping. On injecting steam in latter compartments facilitate further removal of ammonia in the range of 44 to 48%. The reduction of dissolved solids in the effluents from different compartments, indicating release of ammonia nitrogen into atmosphere. Increase in concentrations of suspended solids in the effluent was mostly due to addition of chopped rice straw which floats on water surface and escape through effluent.

Insignificant increase in nitrite and nitrate concentrations in effluent from various compartments of urea biohydroliser indicate that nitrification of ammonia was not taking place. The slow build up of nitrite and nitrate concentrations in the lagoons indicating nitrification of ammonia during wastewater stabilization. The urea concentration in lagoon effluent was reduced due to the presence of ureolytic bacteria present in septic tank effluent in lagoons. As algae- chlorella present in lagoons by virtue of addition of algal culture, utilize ammonia nitrogen and other nitrogen species from wastewater, thereby reduction of ammonia nitrogen was observed. The concentrations of COD and BOD was also reduction significantly. The characteristics of final treated effluent being discharged into river conformed to the discharge standards prescribed by regulatory agencies into inland surface water.

Conclusions

Based on the studies on full scale urea bio-hydrolyser plant to treat urea bearing wastewater, it was concluded that ureolytic bactria *Bacillus pasteurii* could hydrolyse 85 to 90 percent urea from wastewater. Urea hydrolysis process was brisk at initial period of 30 hours, hydrolyzing around 70 to 73 percent urea in the first six compartment of the bio-hydrolyser plant. Ammonia nitrogen produced during urea bio-hydrolysis could be stripped off at pH 10.2 + 0.2 without applying mechanical means. Injecting pressurized steam at the bottom of latter compartments facilitate 44 to 48 percent ammonia removal by stripping. Paddy straw, an agricultural residue can profitable be used as an carbon source for microorganisms as against costly chemicals like methanol and other organics. Ammonia nitrogen trapped in the form of in-organics further nitrified in lagoons with the help of microorganisms into nitrate via nitrite. Algae-*chlorella* present in lagoons reduce ammonia nitrogen and nitrate nitrogen from the wastewater. Nitrate nitrogen was denitrified by microorganisms into nitrogen gas to obtain nitrogen free wastewater. BOD and COD was also reduced in the lagoons.

Urea bio-hydrolyser cum stripper reduces significant concentration of urea and ammonia in the wastewater from nitrogenous fertilizer industry to conform standards prescribed by regulatory agencies for discharge of treated effluent into inland surface water.

References

APHA-AWWA-WPCF 1989. *Standard Methods for the Examination of Water and Wastewater*, 17^{th} Edition, American Public Health Association, Washington, DC.

Evans, W. H. David, E. J. and Patterson, S. J. 1973. Bio-degradation of urea in river water under controlled laboratory conditions. *Water Res.* **7, 975.**

Gillette, L. A., Miller, D. L. and Redman, H. E. 1952. Appraisal of Chemical waste problem by fish toxicity tests. *Sewage and Industrial Waste.* **24, 1397.**

India 1995. A reference Annual, Published by Ministry of Information and Broadcasting. Government of India, pp. 545-546.

IS : 9841. 1981. *Guide for treatment and Disposal of Fertilizer Industry*, Indian Standards Institution, New Delhi.

Monthly Review of Indian Economy 1997. Economy Intelligence Service Series, 1997, Published by Center for Monitoring Indian Economy (CMIE) Pvt. Ltd., February, 1997. **pp . 58.**

Watt, G. W. and Chrisp, J. D. 1954. Spectrophotometric method for determination of urea. *Anal. Chem.* **26, 452.**