Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(5): 889-900

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Removal of ammonia from polluted waters using new bio-sorbents

K. Prameela Rani and K. Ravindhranath*

Department of Engg. Chemistry and Post Graduate Chemistry, Bapatla Engineering College (Autonomous), Bapatla, Guntur Dt., A.P., India

---

ABSTRACT

The bio-sorbents derived from leaves of Achyranthes aspera, Hsibisuc rosa-sinensis and Tribulus terrestris have been studied for their sorption nature towards ammonia from polluted waters with respect to various physicochemical parameters such as pH, sorbent concentration and equilibration time. The conditions for maximum removal of Ammonia from polluted waters have been optimized. The interference of common anions and cations that present in natural waters on the % of extraction of ammonia under optimum conditions has been studied. It is found that anions like Chlorides, Fluorides, Sulphate, Phosphate and Carbonates have marginal interferenc while Cations like Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} interfered to some extent. The adoptability of the methodologies developed in this work are tested with diverse samples collected from industrial effluents and naturally existing polluted lakes and it is found that the procedures are remarkably successful in removing the substantial amounts of ammonia from waste waters.

Key words: Ammonia, pollution control, bio-sorbents, applications

---

INTRODUCTION

Anaerobic biological degradation of nitrogenous matter present in wastes waters causes the contamination of water bodies with ammonia. Ammonia is toxic and it causes headache, insomnia, nausea, diarrhea and a failure in glucose tolerance in animals and human beings. [1-9]. It attacks the cardiac tissues [10, 11] and also causes metabolic toxicity by interfering with energy metabolism in the brain [12]. Aaquatic life is also disturbed due to the presence of ammonia in water bodies and ammonia is recognized as strong cell poison and can cause damage to the gills of fish even at levels of 0.25ppm. Accelerated eutrophication of lakes, depletion of dissolved oxygen in water bodies and loss of valuable aquatic species due to decrease in dissolved oxygen are other deleterious effects of ammonia pollution [7].

The potential source of contamination water bodies due to nitrogenous matter are public, industrial and agricultural wastes [1-4]. Aanimal feeds, food additives, cleaning agents and effluents from the industries manufacturing fibers, plastics, explosives, paper, and rubber are some of the worth mentioning sources. Further ammonia is also a metabolic by-product of fish [5].

The maximum limit of ammonia set by the European Association for drinking water is approximately 0.5 ppm and also a guide level is given as 0.05ppm [13, 14]. The raw water with high ammonia concentration must therefore be treated before it reaches the consumer and also the wastewater discharge into the receiving water.

Air stripping, ion exchange, and biological nitrification and denitrification are the more conventional methods in practice [15]. Biological nitrification and denitrification methods are limited to a minimum 5 ppm of concentration due to the formation of undesirable chemical compounds. The ion exchange methods [16-21] are preferred over the other methods since they are stable, suit automation and quality control and are easy to maintain. Clilnoptilolite zeolites are used in the control of ammonia [21].

Recent interest is also focused on the using Microwave radiation for the control of ammonia [21-25]. New concepts of microbial treatment processes for the removal of ammonia have been discussed by Schmidt I et al (2003) [26]. M.S. Çelik et al (2001) studied the removal of ammonia by natural clay minerals using fixed and fluidized bed column reactors [27].

These methods involve large expenditure and so investigations are being made to explore the sorption potentialities of bio-wastes of flora and fauna origin as alternative methods in controlling pollution [28-32]. V. Parimala et. al (2007) investigated the removal of ammonia using low cost agricultural wastes [32]. Duck weeds [28], neem products [29] and low cost agricultural wastes [30, 32] have been explored for the removal of ammonia from polluted waters. These methods based on the use of waste materials as bio-sorbents are proving to be potential alternative to the existing costly methods for the removal of ammonia.

The endeavor of the present work is to explore the sorption potentialities of thermally activated powders of leaves and barks of some plants in controlling the concentrations ammonia in polluted waters by studying the sorption characteristics of these bio-sorbents under various physicochemical parameters such as pH, sorbent concentration and time of equilibration.

EXPERIMENTAL SECTION

(A) Chemicals: All chemicals used were of analytical grade.

1. **500 ppm stock solution of Ammonia** was prepared by dissolving suitable amounts of Ammonium chloride in double distilled water and is suitably diluted as per the need.

2. **Nessler's reagent:** 35gs of Potassium Iodide and 4% Mercuric Chloride were dissolved in 100 ml of double distilled water with constant stirring until a slight red precipitate remains. To this, solution of NaOH (120gms of NaOH + 250 ml of double distilled water) was added and made up to 1 lit with double distilled water .A little more Mercuric Chloride solution was added until there was a permanent turbidity . The mixture was allowed to stand for one day and decant from the sediment. The solution was kept in stoppered dark colored bottle.

(B) Adsorbents:

Thermally activated powders of leaves and their ashes of many plants have been employed in this work. It is found that leaves or stems or their ashes of *Achyranthes aspera*, *Hsibisuc rosa-sinensis and Tribulus terrestris* have been found to have affinity towards ammonia and hence the methodologies presented here, pertain to these sorbents only.

Achyranthes aspera ***Hsibisuc rosa-sinensis*** ***Tribulus terrestris***

Fig 1: Plants showing affinity towards Ammonia

Achyranthes aspera is a species of plant in the Amaranthaceae family and is distributed throughout the tropical world and it has medicinal and therapeutic values. Further, it has religious sanctitity and it is used in Hindu rites.

Hsibisuc rosa-sinensis is an ever green flowering shrub belongs to *Malvaceae family* and is grown throughout tropics and subtropics.

Tribulus terrestris is a flowering plant in the family of Zygophyllaceae and is grown in warm temperate and tropical regions. It has medicinal values and is widely used in traditional medicines.

Sorbent Preparation:
The leaves of *Achyranthes aspera, Hsibisuc rosa-sinensis and Tribulus terrestris* were cut or scrapped freshly, washed with tap water, then with distilled water and then sun dried. The dried materials were powdered to a fine mesh of size < 75 µ and activated at 105^0 C for 4 hrs. in an oven and then these were employed in this work. Further, the leaves of the said plants were burnt to ashes and their ashes were also used as sorbents in this work.

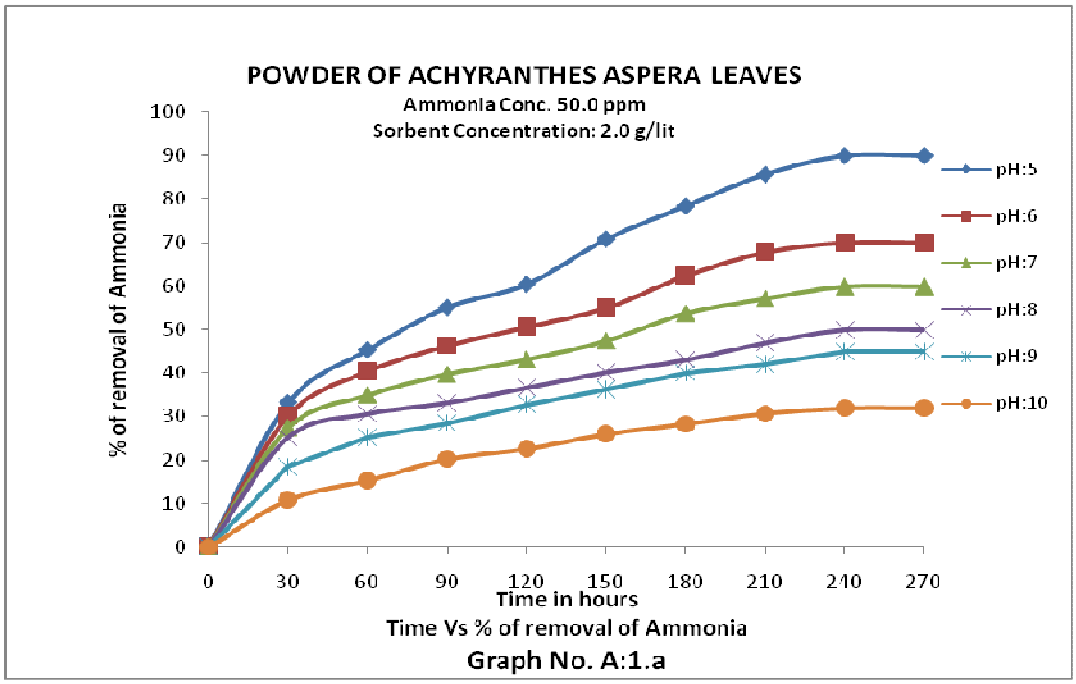
(C) Adsorption experiment:
Batch system of extraction procedure was adopted [33-35]. Carefully weighted quantities of adsorbents were taken into previously washed l lit/500 ml stopper bottles containing 500ml/250ml of Ammonium Chloride solution of predetermined concentrations. The various initial pH values of the suspensions were adjusted with dil. HCl or dil. NaOH solution using pH meter. The samples were shaken in mechanical shakers for a desired period and after the equilibration period; an aliquot of the sample was taken for Ammonia determination. Ammonia was determined by using Nessler's method spectrophotometrically [36].

(D) Estimation of Ammonia:
An aliquot amount of ammonium chloride solution was taken in a 50ml volumetric flask. To it 1ml of Nessler's reagent was added, mixed well and was allowed to stand at least 10 min at room temp in a diffused light. The solution was diluted to the volume and mixed well. Optical Density of the orange-brown color was measured at 525 nm against a reagent blank using U.V and visible Spectrophotometer (of Systronics make). Thus obtained O.D Value was referred to standard graph (drawn between O.D and Concentration) prepared with known amounts of ammonia to find concentration of unknown solutions.

(E) Effect of Interfering Ions:
The interfering ions chosen for study are the common ions present in natural waters, viz., Sulphate, Nitrate, Chloride, Phosphate, Fluorides, Carbonate, Calcium, Magnesium, Copper, Zinc and Nickel. The synthetic mixtures of Ammonia and one of the interfering ions were so made that the concentration of the interfering ions maintained at ***five*** fold excess than the ammonium ion concentration. 500 ml of these solutions were taken in stopped bottles and then correctly weighed optimum quantities of the promising sorbents were added. Optimum pH was adjusted with dil. HCl or dil. NaOH using pH meter. The samples were shaken in shaking machines for the desired optimum periods and then the samples were filtered and analyzed for Ammonia. % of extraction was calculated from the data obtained. The results are presented in the Table No. 1.

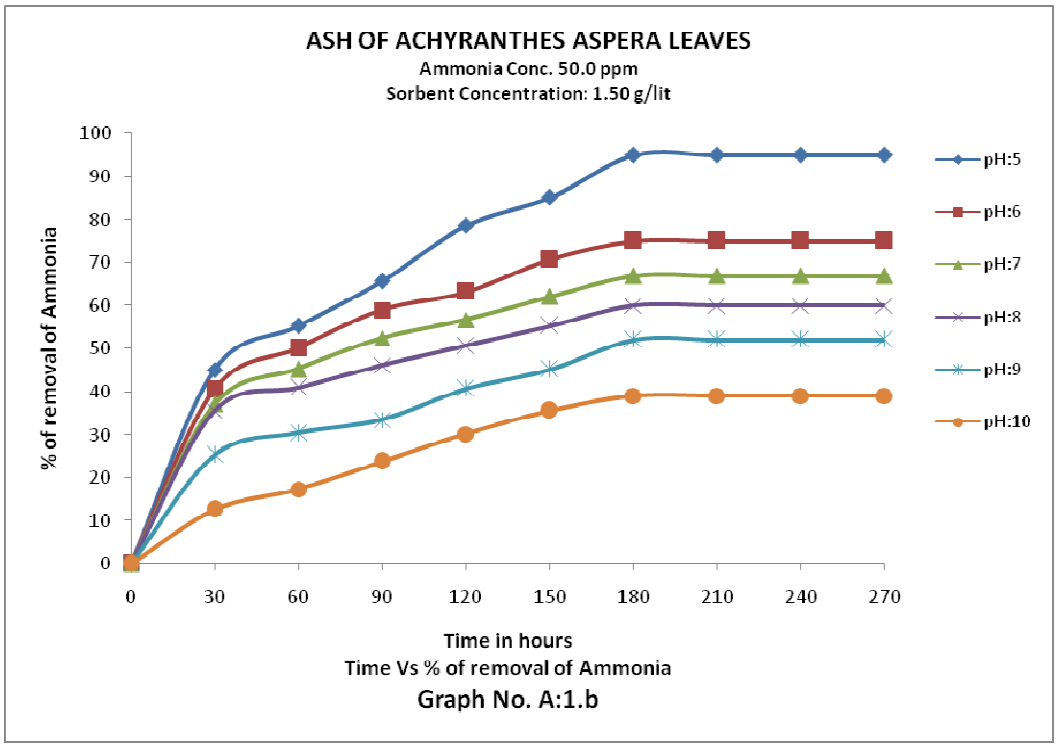
(F)Applications of the developed bio-sorbents:
The adoptability of the methodology developed with the new bio-sorbents in this work for removing ammonia is tried with some real sewage/effluent samples of some industries and natural samples. For this purpose, samples were collected from the effluents of Paper pulp industry at Rajahmundry, Sugar industry at Tadepalligudem and Dairy form at Guntur in Andhra Pradesh. Further, three samples were collected at different polluted lakes in Bapatla mandalam of Guntur District of Andhra Pradesh.

Then these samples were subjected to extraction for Ammonia using the bio-sorbents developed in this work at optimum conditions of pH, equilibration time and sorbent concentration. The results obtained were presented in the Table 2.



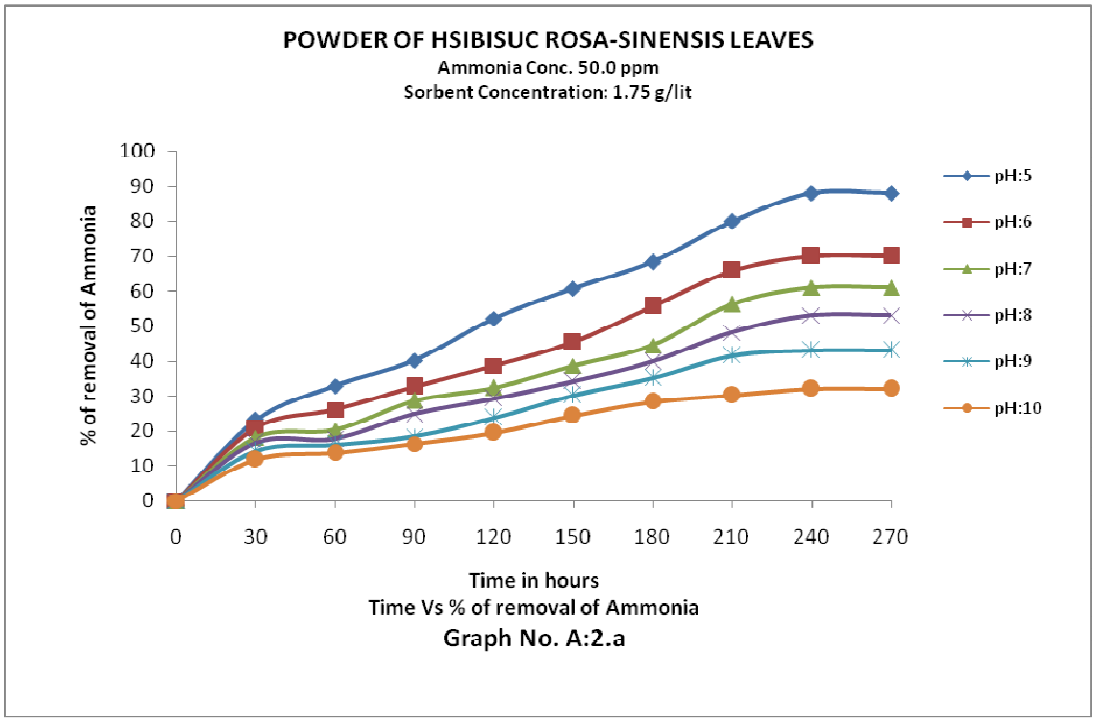
Time Vs % of removal of Ammonia

Graph No. A:1.a



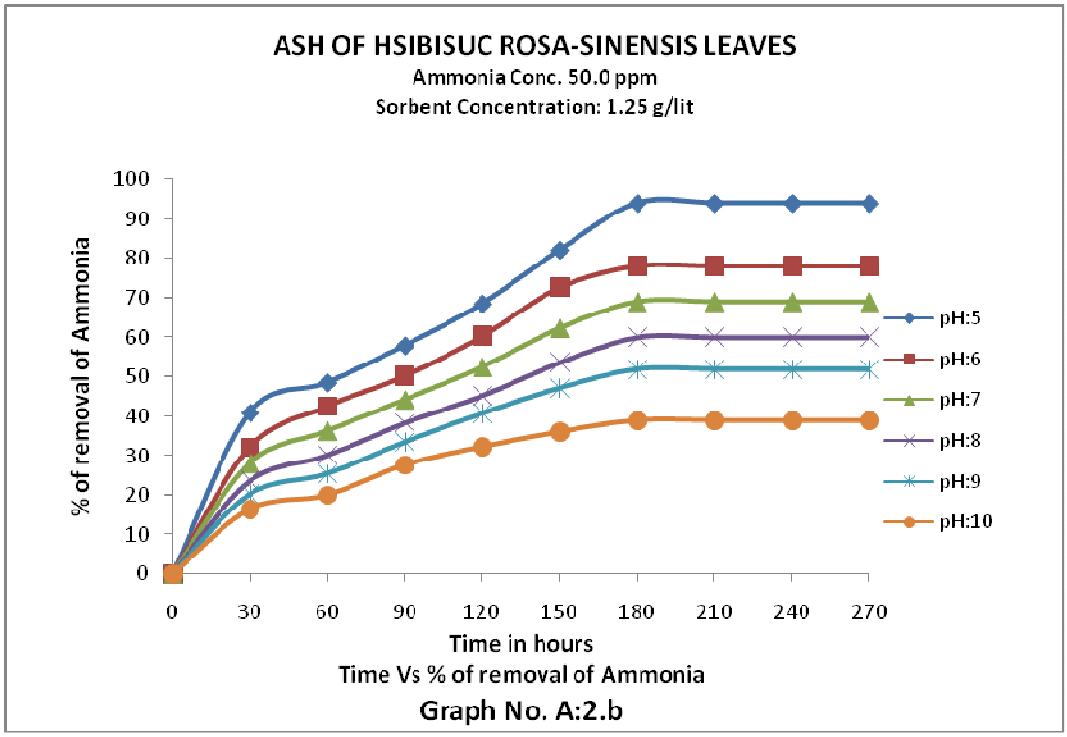
Time Vs % of removal of Ammonia

Graph No. A:1.b



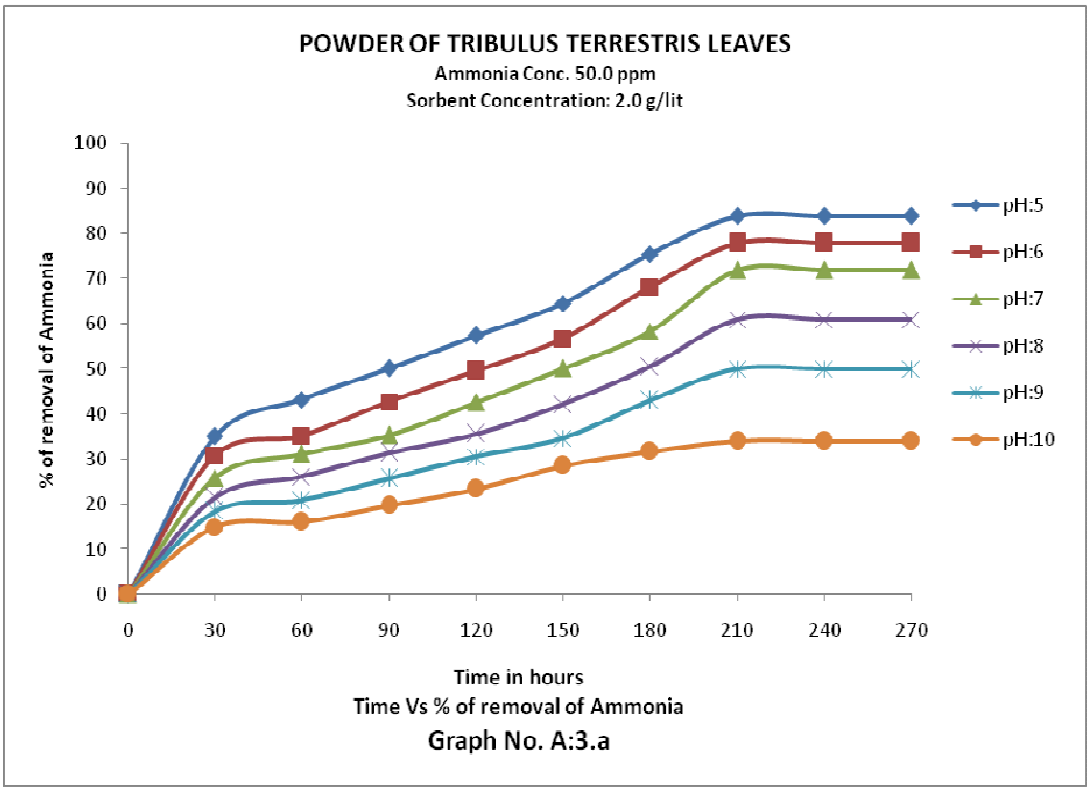
Time Vs % of removal of Ammonia

Graph No. A:2.a

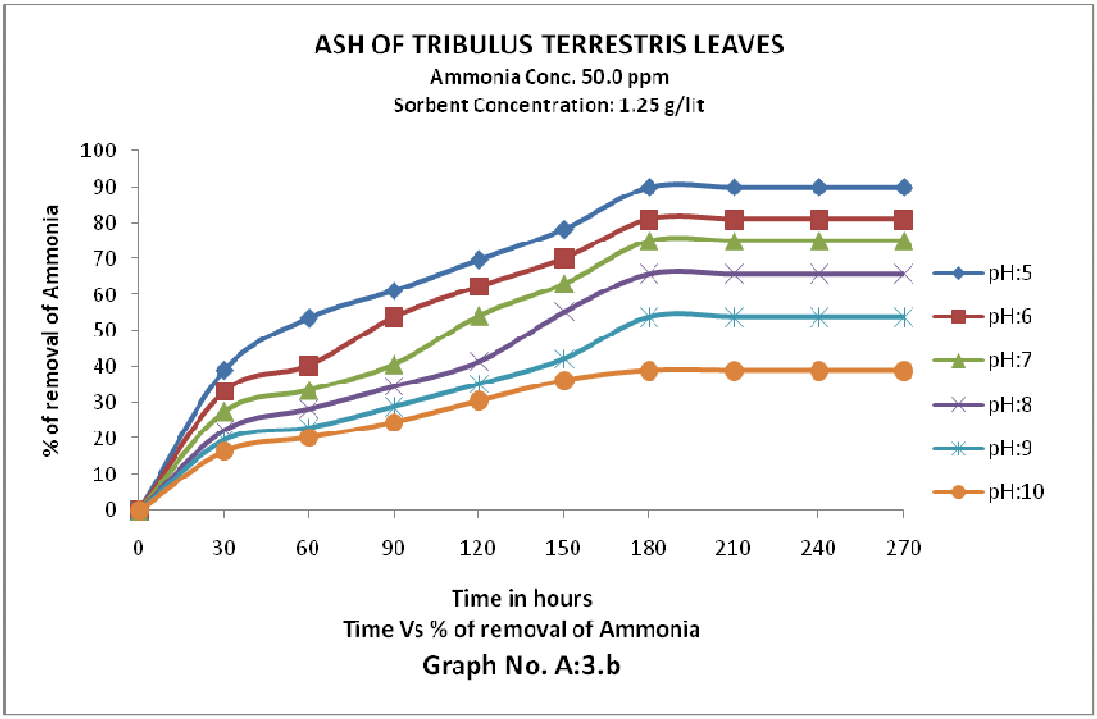


Time Vs % of removal of Ammonia

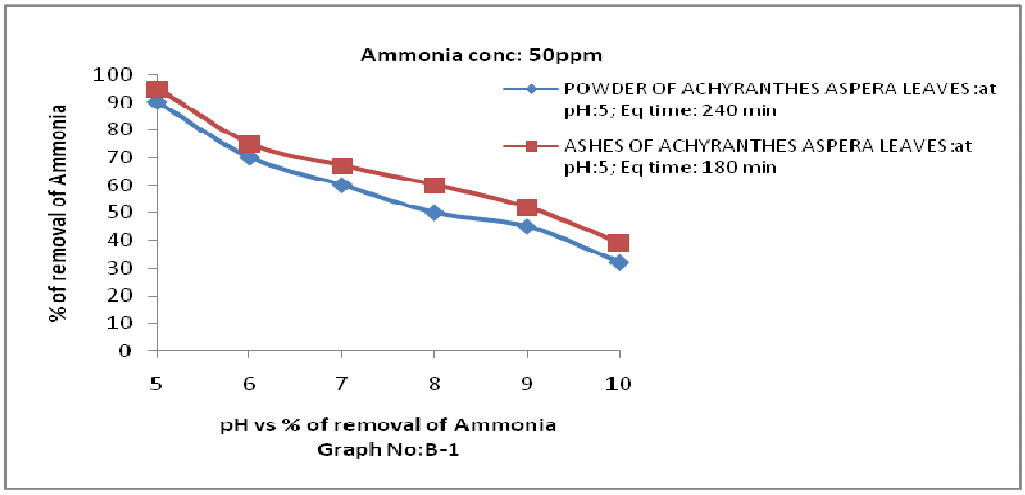
Graph No. A:2.b

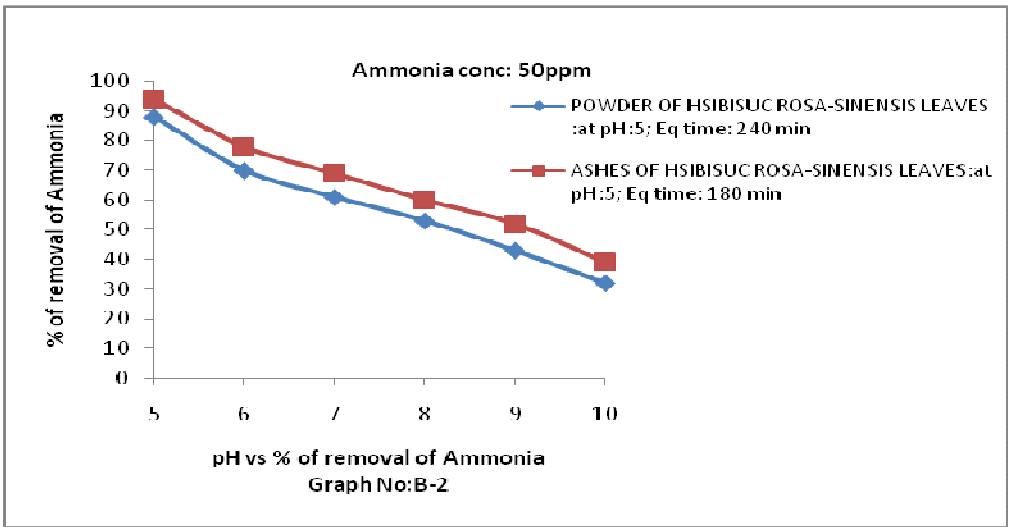


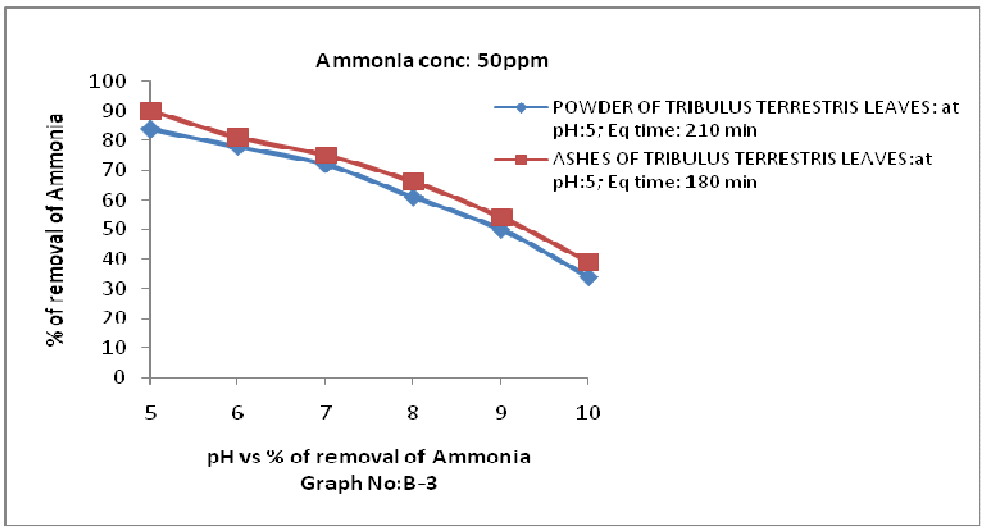
Graph No. A:3.a

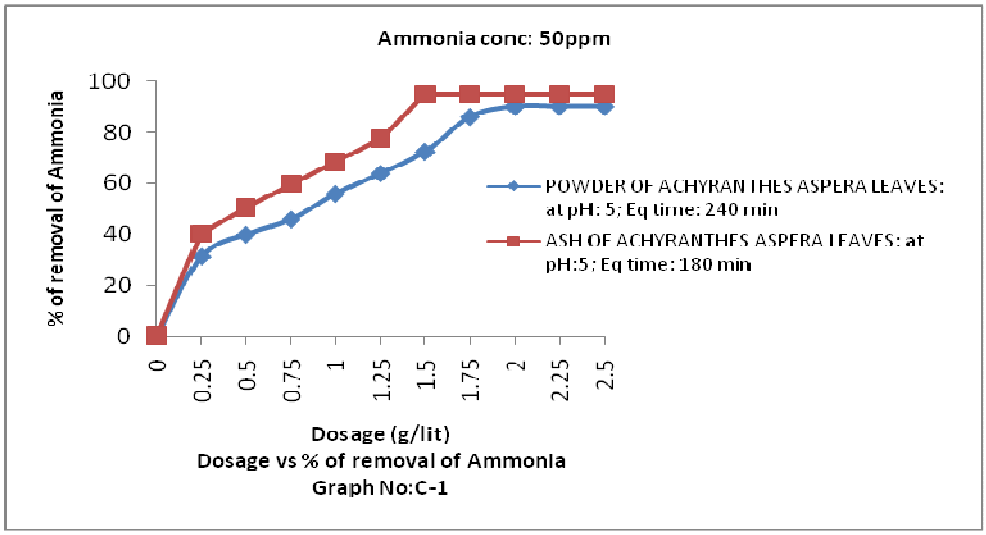


Graph No. A:3.b

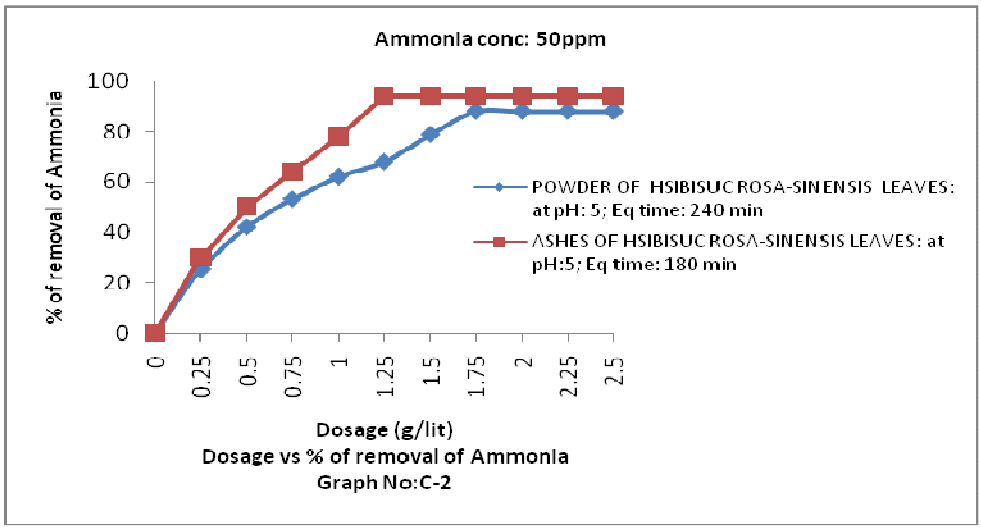

Ammonia conc: 50ppm
POWDER OF ACHYRANTHES ASPERA LEAVES :at pH:5; Eq time: 240 min
ASHES OF ACHYRANTHES ASPERA LEAVES :at pH:5; Eq time: 180 min
% of removal of Ammonia
100
90
80
70
60
50
40
30
20
10
0
5
6
7
8
9
10
pH vs % of removal of Ammonia
Graph No:B-1


Ammonia conc: 50ppm
POWDER OF HSIBISUC ROSA-SINENSIS LEAVES :at pH:5; Eq time: 240 min
ASHES OF HSIBISUC ROSA-SINENSIS LEAVES :at pH:5; Eq time: 180 min
% of removal of Ammonia
100
90
80
70
60
50
40
30
20
10
0
5
6
7
8
9
10
pH vs % of removal of Ammonia
Graph No:B-2

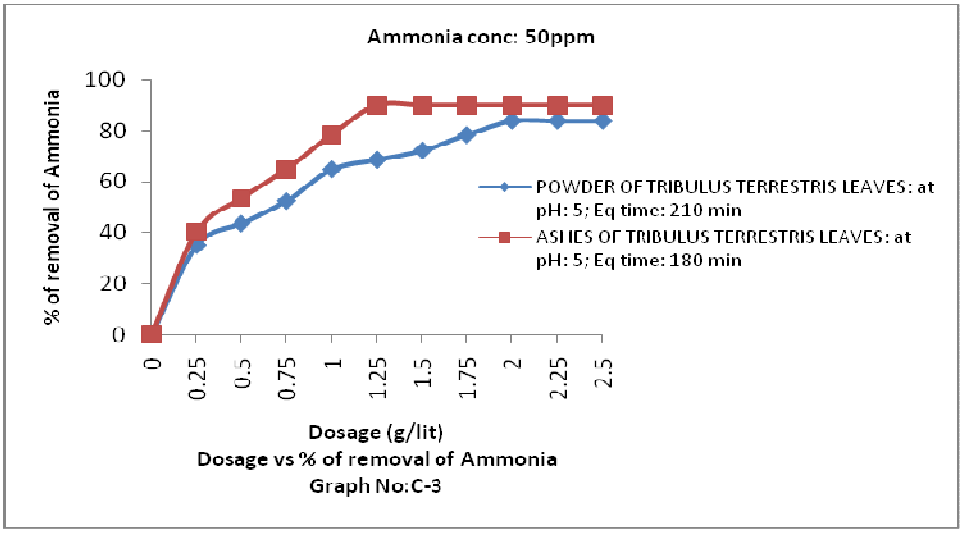

Ammonia conc: 50ppm
POWDER OF TRIBULUS TERRESTRIS LEAVES: at pH:5; Eq time: 210 min
ASHES OF TRIBULUS TERRESTRIS LEAVES :at pH:5; Eq time: 180 min
% of removal of Ammonia
100
90
80
70
60
50
40
30
20
10
0
5
6
7
8
9
10
pH vs % of removal of Ammonia
Graph No:B-3



Dosage vs % of removal of Ammonia
Graph No:C-1



Dosage vs % of removal of Ammonia
Graph No:C-2



Dosage vs % of removal of Ammonia
Graph No:C-3

RESULTS AND DISCUSSION

The powders of leaves and their ashes of *Achyranthes aspera, Hsibisuc rosa-sinensis and Tribulus terrestris* have been found to have affinity towards ammonia. The percentage removal of ammonia is studied under various parameters viz., pH, time of equilibration and adsorbent dosage, with these bio-sorbents. The results obtained are presented in the Graph No: A: 1-3; B: 1-3; C: 1-3 and in Table No. 1&2.

The following observations are significant:

1. % of extractability increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability remains constant, i.e. an equilibrium state has been reached (vide Graph Nos: A: 1-3). As for example with activated leaves powder of *Achyranthes aspera as adsorbent, the % of extraction at pH: 5 is found to be 33.2% at 30 min of equilibration, 45.3% at 60 min, 55.1% at 90 min and 60.4% at 120 min, 70.8% at 150 min, 78.4% at 180 min 85.7% at 210 min 90.0% at 240 min or above (vide Graph No. A: 1.a). Similarly with activated leaves powder of Hsibisuc rosa-sinensis the % of extraction at pH: 5 is found to be: 23.1% at 30 min, 32.8% at 60 min, 40.2% at 90 min, 52.1% at 120 min 60.7% at 150 min, 68.3% at 180 min 79.9% at 20 min , 88.0% at 240 min or above (vide Graph No. A: 2.a). At pH: 5 % of extraction has been found to be 35.1% at 30 min, 43.3% at 60 min, 50.2% at 90 min, 57.4% at 120 min 64.6% at 150 min 75.5% at 180 min 84.0% at 210 min or above for activated leaves powder of Tribulus terrestris (vide Graph NO A: 3.a).Similar observations have been found with the ashes of above activated leaves and the results are presented in vide Graph No's. A: 1.b, 2.b and 3.b.*

2. **pH sensitivity**: The % of extraction is found to be pH sensitive. The % of extractability of ammonia increases with time and decreases with the increase of pH for a fixed adsorbent concentration. (Vide Graph No. : A: 1-3; B: 1-3). The optimum pH has been found to be 5.

As for example, with the leaves powders of *Achyranthes aspera as adsorbent*, the maximum extractability is found to be: 32.0 % at pH: 10; 45.0% at pH: 9; 50.0% at pH: 8; 60.0% at pH: 7; 70.0 % at pH: 6; and 90.0% at pH:5. With the Ash of *Achyranthes aspera leaves*, the maximum extractability is found to be : 39.0% at pH:10; 52.0% at pH:9; 60.3% at pH:8; 67.4% at pH:7; 75.6% at pH:6 and 95% at pH:5. At equilibration pHs: 10, 9,8, 7,6 and 5, % of maximum extraction has been found to be respectively 32.2%, 43.6 % ,53.1% , 61.3% , 70.8% and 88.0% with the activated leaves powder of *Hsibisuc rosa-sinensis* and 39.7%, 52.2% , 60.8% , 69.8% , 78.8% and 94.0% with the Ash of *Hsibisuc rosa-sinensis* leaves as adsorbent. With Adsorbent derived from *Tribulus terrestris* leaves powder, the extractability is found to be 34.8% at pH:10; 50.3% at pH:9; 61.1% at pH:8.; 72.6% at pH:7; 78.5% at pH: 6 and 84.0% at pH:5 and with the Ash of *Tribulus terrestris* leaves the maximum extractability is found to be 39.1% at pH: 10; 54.4% at pH: 9; 66.2% at pH: 8; 75.7% at pH:7; 81.2% at pH: 6 and 90.0% at pH:5.

3. The % of maximum extraction of ammonia is found to be more in the case of Ashes as sorbents than powders of leaves at the optimum conditions of pH, time of equilibration and sorbent dosage. Moreover, the optimum time of equilibration needed for maximum removal of ammonia is also found to be less in the case of Ash than powders of leaves. As for example, the maximum extractability of ammonia is 90% percent at pH: 5 after an equilibration period of 240 min with the sorbent concentration of 2 g/lit for Achyranthes aspera leaves powders while with its Ash, the extractability is found to be found to be enhanced to 95% at pH: 5 after an equilibration period of only 180 min with the sorbent concentration of 1.5 g/l. In the case of adsorbent derived from leaves of Hsibisuc rosa-sinensis, the % of extractability is found to be 88% at pH: 5 after an equilibration period of 240 min with the sorbent concentration 1.75 g/lit for activated powder while with its Ash the extraction has been increased to 94% at pH: 5 after an equilibration period of only 180 min and sorbent concentration 1.25 g/lit. With leaves powders of Tribulus terrestris, 84% of extraction of ammonia is found at pH:5 at an equilibration period of 210 min and sorbent concentration of 2.0 g/lit while with its Ashes, 90% of extraction is found at pH:5, equilibration period of 180 min and with sorbent concentration of 1.25 g/lit.

4. When percentage removal is studied with respect to adsorbent dosage at fixed optimum pH: 5 and at optimum equilibration times, the graphs increase up to certain dosage and from then onwards plateaus are obtained. The optimum sorbent dosage needed for the adsorbents derived from ashes is less than their respective adsorbents derived from raw powders of the leaves. As for example, with powders of leaves of Achyranthes aspera, the optimum sorbent dosage is found to be 1.75gm/lit while with their ashes only 1.5g/lit is adequate at optimum conditions of pH:5 and equilibration times (vide Graph Nos: C-1). The optimum sorbent dosage is found to be 1.75gm/lit for Hsibisuc rosa-sinensis leaves powders while 1.25g/lit for their Ashes at optimum conditions of

equilibration (vide Graph Nos::C-2). With Tribulus terrestris leaves powders, the optimum sorbent dosage is found to be 2.0gm/lit while with their ashes is found to be :1.25g/lit at the optimum conditions of equilibration (vide Graph Nos::C-3).

D: EFFECT OF INTERFERING IONS:

The extractions of Ammonia in presence of fivefold excess of the common ions found in natural waters, namely Chloride, Fluoride, Sulphate, Phosphate, Carbonate, Calcium, Magnesium, Copper and Zinc ions have been studied with the successful adsorbents at optimum conditions of pH:5 and time of equilibration and sorbent concentration as cited in the Table 1. The results are presented in the Table 1. The following observations are significant:

a. Cations namely, Ca^{2+}, Mg^{2+}, Cu^{2+}, $Zn^{2+}$and Ni^{2+} ions are interfering with the % of extraction to some extent but in no case, % of extraction has come below 61.0%

b. Anions of the present study viz., Chlorides, Fluorides, Sulphate, Phosphate and Carbonates are found to marginally affect the % of extractability of Ammonia under optimum experimental conditions.

DISCUSSION

The scope of the present study does not permit to establish sound theoretical grounds for each observation made and infact, detailed investigations, are needed to account for the observations.

However, the sorption characteristics of the adsorbents for ammonia may be generally viewed as follows:

- Ammonia exists in aqueous solution as either ammonium ion (NH_4^+) or ammonia gas depends upon the pH of the solution. Below pH: 9.25, the predominant species is NH_4^+ and above pH: 9.25, ammonia, NH_3, is considerable. In the present work, studies are made in the pH range from 5 to 10.

- The adsorbents derived from Lingo celluloses have weak ion affinity in the pH range of interest i.e. from 5 to 10. As pH decreases from 10 to 5, the equilibrium shifts towards the formation more and more NH_4^+ species, and thus formed positively charged species get exchanged to the sorbents and thereby progressively increasing the % of extraction. At high pH values, the predominant species is NH_3 and the species being neutral is uninfluenced by the electrostatic thrusts prevailing on the surface of the sorbent and hence, % of extraction decreases.

Table No: 1: Effect of interfering Ions on the Extractability of Ammonia with different Bio-sorbents

S.N	*Adsorbent and its concentration*	*Maximum Extractability at optimum conditions*	*% of Extraction of Ammonia in presence five fold excess of interfering ions at optimum conditions: Conc. of ammonia: 50 ppm at pH:5*										
			SO_4^{2-}	NO_3^{2-}	Cl^-	PO_4^{3-}	F^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}
1	Powder of ***Achyranthes aspera*** *l*eaves:2.0 gms/lit	90.0%; pH:5, 240 min	82.0 %	83.2%	84.2%	87.0%	86.0%	82.5%	67.5%	74.0%	68.0%	63.0%	66.0%
2	***Ashes of Achyranthes aspera*** leaves ;1.5gms/lit	95.0% pH:5, 180 min	83.1%	84.0%	85.0%	88.1%	92.0%	89.5%	83.1%	80.0%	78.5%	83.0%	80.0%
3	Powder of ***Hsibisuc Rosa-sinensis*** *l*eaves:1.75 gms/lit	88.0%; pH:5, 240 min	79.2%	81.4%	83.7%	86.5%	85.2%	81.3%	67.1%	73.8%	67.6%	62%	65.4%
4	***Ashes of Hsibisuc Rosa-sinensis*** leaves ;1.25gms/lit	94.0% pH:5, 180 min	82.6%	83.2%	84.6%	87.2%	91.8%	88.0%	82.4%	79.2%	77.6%	82.1%	78.9%
5	Powder of **Tribulus terrestris** *l*eaves:2.0 gms/lit	84.0%; pH:5, 210 min	78.2%	80.0%	82.8%	86.0%	84.1%	80.3%	65.8%	72.3%	65.8%	61.2%	64.2%
6	***Ashes of*** **Tribulus terrestris** leaves ;1.25gms/lit	90.0% pH:5, 180 min	81.8%	82.4%	84.1%	87.1%	90.2%	84.6%	80.9%	77.5%	73.2%	81.2%	77.6%

Applications:

The Applicability of the methodologies developed in this work have been tested with respects to the real samples of diverse nature, collected from the sewages/effluents of Paper pulp industry, Sugar Factory and also in natural polluted lakes. *The results have been presented in the Table No: 2.*

It is found that the sorbents developed in this work are successful in removing Ammonia at optimum conditions of pH, equilibration time and sorbent dosage. % removal of Ammonia is found to be: 90.2% to 96.1% with leaves powder of Achyranthes aspera and 92.6% to 98.1% with their ashes ; 81.2% to 84.2% with leaves powder of Hsibisuc rosa-sinensis and 85.5% to 88.2 % with their ashes; 80.4% to 83.2% with the leaves powder of Tribulus terrestris and 83.9% to 85.5% with their ashes.

Table No.2: % of Extractability of Ammonia in Diverse Samples

Bio-sorbents	% of Extraction of Ammonia in diverse Samples (actual Conc. of Ammonia is shown in parenthesis)					
	Sample:1: Paper pulp Industry at Rajahmundry, A.P. (12.5 ppm)	Sample:2: Sugar Factory effluents at Tadepalligudem in A.P. (21.5 ppm)	Sample:3: Dairy farm effluents in Guntur,A.P. (14.5 ppm)	Natural polluted Lake samples: in Bapatla mandalam of A.P.		
				Sample-4 (21.5ppm)	Sample-5 (18.5 ppm)	Sample-6 (15.8ppm)
Powder of ***Achyranthes aspera*** leaves concentration:2.0 gms/lit	92.0 %	93.2%	90.2%	96.1%	95.1%	94.2%
Ashes of Achyranthes aspera leaves concentration:1.5gms/lit	93.8%	94.4%	92.6%	98.1%	96.0%	95.2%
Powder of ***Hsibisuc Rosa-sinensis*** leaves concentratio:1.75 gms/lit	84.2%	81.7%	81.2%	83.0%	84.0%	82.1%
Ashes of Hsibisuc Rosa-sinensis leaves concentration:1.25gms/lit	86.7%	86.8%	88.2%	86.5%	86.2%	85.5%
Powder of ***Tribulus terrestris*** *leaves concentratio:2.0 gms/lit*	82.1%	83.0%	80.5%	80.4%	82.7%	83.2%
Ashes of **Tribulus terrestris** leaves concentration:1.25gms/lit	85.2%	84.6%	85.5%	84.6%	84.3%	83.9%

CONCLUSION

- The importance of bio-adsorbents such as leaves and barks in removing/controlling Ammonia from polluted waters is brought to the lime light.
- 90.0%, 88.0% and 84.0% of removal ammonia are found with powders of leaves of *Achyranthes aspera, Hsibisuc rosa-sinensis and Tribulus terrestris; and 95.0*%, 94.0% and 90.0% with their ashes respectively at pH: 5, equilibration time respectively of 240 min, 240 min, 210 min for powders of leaves and 180 min for their ashes at optimum sorbent concentration.
- The minimum sorbent dosage needed for the maximum removal of Ammonia is found considerably less for ashes than for powders of leaves.

- **Interference**:

Anions like Chlorides, Fluorides, Sulphate, Phosphate and Carbonates showed marginal interference while cations like Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} interfered to some extent . However, the % of extractability of Ammonia is found to be considerable. The methodologies developed in this work with the different bio-sorbents are found to be remarkably successful.

Acknowledgement
The authors thank UGC for financial aid for conducting this research work.

REFERENCES

[1] Metcalf and Eddy., Wastewater *Engineering: Treatment of Reuse*. 4th. Ed McGraw Hill Co., New York, **2003**.
[2] McKee, J.E and H.W. Wolf,. (Editors) *Water quality criteria*. 2nd edition. Publ. No.3-A, State Water Quality Control Board, Sacramento, CA. **1963** ,132.
[3] US. Environmental Protection Agency, *Quality Criteria for Water*. Washington, DC. **1976**, 16.
[4] Luebs, R.E. and Laag, A.E. *Calif. Agric.*, **1973**, 27(2); 10.
[5] *Hazardous Substances Data Bank*: Ammonium Chloride, Bethesda, M. D., National Library of Medicine, **1990**.
[6] Environment Canada. National inventory of natural and anthropogenic sources and emissions of ammonia (1980) Rep. No. EPS 5/IC/1, *Environmental Protection Programs Directorate*, **1985**.
[7] EPA, Process design manual for nitrogen control *U.S.EPA, Technology Transfer*, **1975**.
[8] Warren, K.S and Schenker,S. *J Physiol*, **1960**, 199:1805.
[9] Keirla, A.M., McGlain, J.J. Bubn, R.W. and Altemeier, W.A. *Arch. Surg*., **1961**, 83:348.

[10] Wilson, R.D., Muhrer, M.E and Bloomfield, R.A. *Comp. Biochem. Physiol*., **1968**, 25; 295.
[11] Berl, S, Takagaki, G.Clarke, D.D. and Waelsch, H. *J Biol. Chem.* **1961**, *237:2562.*
[12] National Research Council. *Drinking Water and Health. Vol.2*. National academy press, Washington, DC,1980.
[13] AWWA, *Water Quality and Treatment*, McGraw Hill Co., New York, **1990**.
[14] Gaspard, M., A. Neveu and G. Martin, *Water Res.*, **1983**, 17 (3):279-288.
[15] Kelly G. *Environmental Engineering*. Maidenhead, England: MC-Graw Hill Publishing Company, **1996**.
[16] Jorgensen, T.C. and Weatherley, T.C. *Water Research* **2003**, 37: 1723-1728.
[17] Koon J. H., and W.J. Kaufman, *J. WPCF* 47 (3): **1975**, 448-465.
[18] Baykal, B.B., Oldenburg, M. And Sekulov, I. *Environmental technology*, **1996**, 17, 717–726.
[19] Sing G and B. Prasad, *Water Environ. Res*., **1997**, 69 (2): 157-161.
[20] Nguyen M.L., Tanner C,C, N Z J F *Agric. Res*. **1998**, 41: 427-46.
[21] A.R. Rehmani, A.H. Mahvi, A.R. Mesdeaghinia A.R and S. Nasseri, I*nternational j of Environmental Science and Technology,* **2004**, *,1 (2), 125-133.*
[22] Lin L, Yuan S, Chen J, Xu Z, Lu X, *J Hazard Mater*. **2008**, 161 (2-3): 1063-8.
[23] Uğurlu M, Karaoğlu MH , *Environ Sci Pollut Res Int*., **2009**, *16(3):265-73.*
[24] Lin L, Chen J, Xu Z, Yuan S, Cao M, Liu H, Lu X. *J Hazard Mater*.**2009**, *15: 168 (2-3): 862-7.*
[25] Lee S, Maken S, Jang JH, Park K, Park, *J. Water Res*, **2006**, 40(5): 975-80.
[26] Schmidt I, Sliekers O, Schmid M, Bock E, Fuerst J, Kuenen JG, Jetten MS, *Microbiol Rev.*, **2003**, 27(4):481-92.
[27] M.S. Çelik, B. Özdemir, M. Turan, I. Koyuncu, G. Atesok and H.Z. Sarikaya, *Water Supply* Vol 1 No1 **2001**, 81–88.
[28] Korner S, Vermaat JE, Veenstra S, *J Environ Qual*. **2003**, 32(5): 1583-90.
[29] K.K. Krishnani , K.O. Joseph, B.P. Gupta, M. Muralidhar, A. Nagavel. *J. Environ Sci Health* A ,**2002**, 37:893-904.
[30]. K.K. Krishnani , B.P Gupta, K.O. Joseph, M. Muralidhar,C. Sarda, A Nagavel, V. Parimala . *Bull Environ Cntam Toxicol* , **2003**, 71:196-203 .
[31] K.K. Krishnani, V. Parimala, B.P. Gupta, I.S., Azad, X. Meng., M. Abraham. *Water Environ Res*. **2006,** 78:938-950.
[32] V. Parimala, K.K. Krishnani, B.P.Gupta, R. Ragunatha, S.M./ Aillai, P. Ravichandran, *Bull Environ, Contam. Toxicol*, **2007**, 78:288-293.
[33] R.K. Trivedy, R.K., "*Pollution Management in Industries*" Environmental Publications, **1979**, KARAD, INDIA .
[34] Metcalf and Eddy.(Editor) , *Wastewater Engineering: Treatment of Reuse*. 4th. Ed., McGraw Hill Co., New York 2003.
[35] Gerard Kiely., *Environmental Engineering*, McGraw-hall International Editions **1998**.
[36] Arthur I. Vogle.. *A text book of Quantitative Inorganic Analysis including elementary Instrumental analysis*, 3rd Ed., ELBS.,**1961**.