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Research Article

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# New bio-sorbents in controling ammonia pollution in wastewaters

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## ABSTRACT

*Ashes of leaves of Phyllanthus niruri , Annona squamosa , Calotropis gigantean, Tridax procumbens , Morinda tinctoria and* Azadirachta indica *have shown strong affinity towards ammonia .The sorption properties of these bio-materials in effecting the removal of ammonia in polluted waters have been explored by optimizing the various physicochemical parameters such as pH, time of equilibration and sorbent concentration. More than 87% removal of ammonia has been observed with these sorbents at pH: 5 and at optimum conditions of time of equilibration and sorbent concentration. The interference of anions like Chlorides, Fluorides, Sulphate, Phosphate and Carbonates, is marginal while cations like* $Ca^{2+}$, $Cu^{2+}$, $Zn^{2+}$ *and* $Mg^{2+}$ *interfere to some extent but, however, the % of extractability of ammonia has never come down 70.0%. The methodologies developed in this work for the removal of ammonia are applied to diverse samples collected from industrial effluents and polluted lakes and it is found that the procedures are remarkably successful.*

**Key Words:** Ammonia, pollution control, bio-sorbents, applications.

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## INTRODUCTION

Removal of ammonia from polluted waters is one of the interesting topics of environmental researchers. Ammonia exists in waters due to incomplete biological degradation of nitrogenous matter [1-4]. Main sources of ammonia pollution are the discharges from municipal, industrial and agricultural sites. Ammonia is also a metabolic byproduct of fish and is a strong cell poison and can cause damage to the gills of fish even at levels of 0.25ppm [5].

Ammonia exists in water either in unionized ammonia ($NH_3$) or ionized ammonia ($NH_4^+$) depending up on the pH and temperature conditions [3, 6]. The toxicity of ammonia to aquatic organisms is attributed to the unionized fraction ($NH_3$) of ammonia. Ammonia causes headache, insomnia, nausea, diarrhea and a failure in glucose tolerance in animals and human beings [8,9]. There is evidence that ammonia targets cardiac tissue [10,11]. Ammonia causes metabolic toxicity and interferences with energy metabolism in the brain [12]. Ammonia pollution in natural water bodies accelerate eutrophication of lakes and this phenomenon results in depletion of dissolved oxygen content in waters and thereby endangering the existence of aquatic life.

The maximum limit of ammonia set by the European Association for drinking water is 0.5 ppm with a guiding level as 0.05ppm [13, 14]. The maximum allowed limit for agricultural waters is 1.0 ppm ; 10 ppm for in feeding waters for municipal waste water treatment methods. Industrial effluents having more than 100 ppm of ammonia are prohibited.

***In view of toxicity of ammonia, efforts are being envisaged to develop methods to control the ammonia.***
The most widely used methods for removing ammonia from wastewater are air stripping, ion exchange, and biological nitrification and de-nitrification [15]. Biological methods are unsatisfactory when there are heavy fluctuations in the concentrations of ammonia in waste waters and further, nitrification and de-nitrification methods are associated with the formation of undesirable chemical compounds. The ion exchange methods [16-21] are preferred over the other methods since they are stable, suitable for automation and quality control and are easy to maintain but involve heavy expenditure.

Recently, interest is being focused on 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) [27] studied the removal of ammonia by natural clay minerals fusing fixed and fluidized bed column reactors.

These methods are costly 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. Parimal 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.

In the present work, the sorption characteristics of ashes of leaves of some herbal plants have been studied for the removal of Ammonia from polluted waters with respect to various physicochemical parameters such as pH, time of equilibration and sorbent concentration and we tried to develop simple methodologies in controlling the Ammonia pollution in waste waters by optimizing the extraction conditions.

## 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 was 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 1lit 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:**
Ashes of leaves of *Phyllanthus niruri* , *Annona squamosa* , *Calotropis gigantean, Tridax procumbens* , *Morinda tinctoria and Azadirachta indica,* have been found to have affinity towards ammonia and hence the methodologies presented here, pertain to these sorbents only.

***Phyllanthus Niruri***

***Annona squamosa***

***Calotropis gigantean***

***Tridax procumbens***

***Morinda tinctoria***

***Azadirachta indica***

Phyllanthus Niruri is an herbal plant belonging to Phyllanthaceae family and is found in Central and Southern India. It has many therapeutic values in curing jaundice, diabetes, dyspepsia, ulcers, sores, swellings, ophthalmia and chronic dysentery. *Annona squamosa is* a small well-branched shrub that bears edible fruits called sugar-apple; belongs to Annonaceae family and grows well in lower altitudes. *Calotropis gigantean* is a species of Calotropis native to South Asian countries and it belongs to Apocynaceae family. It is a large shrub growing upto 3-4 meters tall and its wound healing ability is reported in literature [33].

*Tridax procumbens* is a species of flowering plant in the daisy family and is best known as a widespread weed and pest plant. It grows in tropical, subtropical and mild temperate regions worldwide. It possesses medicinal uses especially for diabetic treatment. The oral administration of leaf extracts at doses of 200 mg $kg^{-1}$ lead to a significant blood glucose reduction. This laid the foundation to study the active compounds of such anti-diabetic plants that are responsible for the hypoglycemic activities [34]. *Morinda tinctoria*, commonly known as *Aal or Indian Mulberry* is a species of flowering plant and belongs to Rubiaceae family and is native to South Asia. It is an evergreen shrub growing to 5-10 m tall. The plant is extensively cultivated in India and its leaves and roots are used in traditional system of medicine [35]. It is reported to have anticonvulsant activity[35]. *Azadirachta indica*, or Neem Tree, is an evergreen tree native to Southeast Asia and it belongs to Meliaceae family.

**Sorbent Prepatration**: The leaves of Phyllanthus Niruri , Annona squamosa, Calotropis gigantean, Tridax procumbens, Morinda tinctoria and *Azadirachta indica,* were cut freshly, washed with tap water, then with distilled water and then sun dried. The dried materials were burnt to ashes and these bio-products were employed in this work.

### (C ): Adsorption experiment :

**Batch system of extraction procedure was adopted.[1,15,37].** 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, filtered and was analyzed for ammonia using Nessler's method spectrophotometrically [38].

**(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 10min at room temp in a diffused light. The solution was diluted to the volume and mixed well. Optical Density (O.D.) 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 a standard graph (drawn between O.D and Concentration) prepared with known concentrations of Ammonia by adopting the method of Least Squares to find concentration of ammonia in unknown solution.

**(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 was 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 tested 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.

## RESULTS AND DISCUSSION

The percentage removal of ammonia is studied under various parameters viz., pH, time of equilibration and adsorbent dosage, with the ashes of leaves of *Phyllanthus Neruri, Annona Squmosa ,Calotropis Zygantia, Tridox Procumbens, Moringa Tinctoria and Azadiracta Indica*. The results obtained are presented in the Graph No: A: 1-6; B: 1 & C: 1 and Table No. 1 &2.

**The following results are significant:**

1. % of extractability of ammonia increases with time for a fixed sorbent at a fixed pH and after certain duration, the extractability remains constant, i.e. an equilibrium state has been reached (vide Graph No:A:1-6). As for example, % of extraction is found to be 60.0% at 1 hr, 75.0% at 2 hrs, 85.0% at 3 hrs, 90.0% at 4hrs, 98.0% at 5 hrs and 98.0% at equilibration times more than 5.0 hrs. with the ashes of leaves of *Annona Squmosa* (vide Graph No.A:2).

2. The % of extractability ammonia is found to be pH sensitive. With decreasing pH, the extractability is found to be increasing for a fixed sorbent concentration. As for example, in the case of ashes of leaves of Phyllanthus nerui, the maximum extractability is found to be: 19.3% at pH: 10, 26.8% at pH: 9; 46.5% at pH: 8; 70.9% at pH: 6 and 99% at pH: 5. In the case of ashes of leaves of Annona Squmosa, the maximum extractability is found to be: 22.8% at pH:10, 39.2% at pH:9; 50.9% at pH:8; 79.2% at pH:6and 98.0% at pH:5. With the Calotropis Zygantia leaves ashes, the maximum extractability is found to be: 19.9% at pH:10, 50.8 %at pH:9;64.3% at pH:8; 69.6% at pH:6and 88.0% at pH:5. Tridox Procumbens leaves ashes extracted ammonia to an extent of: 32.5% at pH: 10, 38.7% at pH: 9; 43.8% at pH: 8; 65.3% at pH: 6and 90.0% at pH: 5. In the case of ashes of leaves of Moringa Tinctoria, the maximum extractability is found to be 21.8% at pH: 10; 38.5% at pH: 9; 48.6% at pH: 8; 68.3% at pH: 6 and 87.0% at pH: 5. The maximum extractability is found to be 27.8% at pH: 10; 38.4% at pH:9; 61.8% at pH:8; 79.8% at pH:6 and 97.0% at pH:5 with the ashes of leaves of Azadiracta Indica.

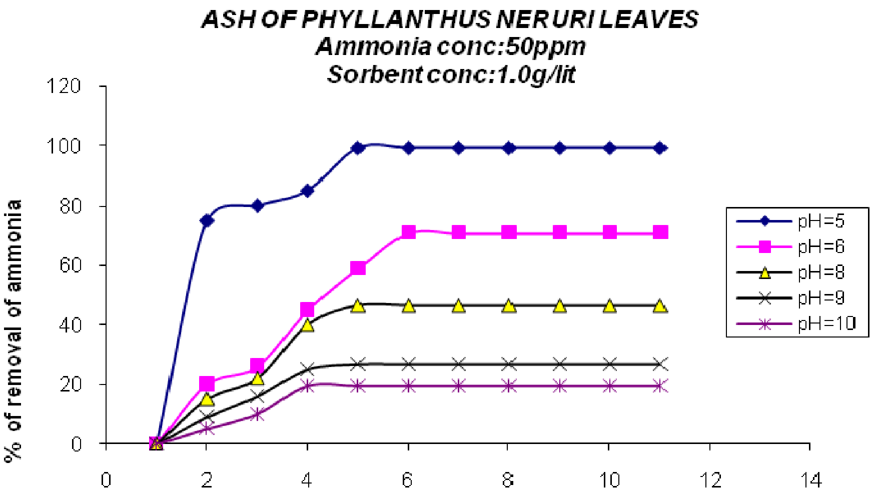
3. The minimum dose of sorbent required for maximum extractability of ammonia at optimum pH values and equilibration time, is found to be : 1 gm/lit for ashes of leaves of Phyllanthus Neruri, Anona Squamosa and Azadiracta Indica; 3gms/lit for ashes of leaves of Moringa Tinctoria , and 4gms/lit for the ashes of leaves of Tridox Procumbens and Calotropis Zygantia. (vide Graph Nos: C: 1)

**D: Effect of interfering ions:**

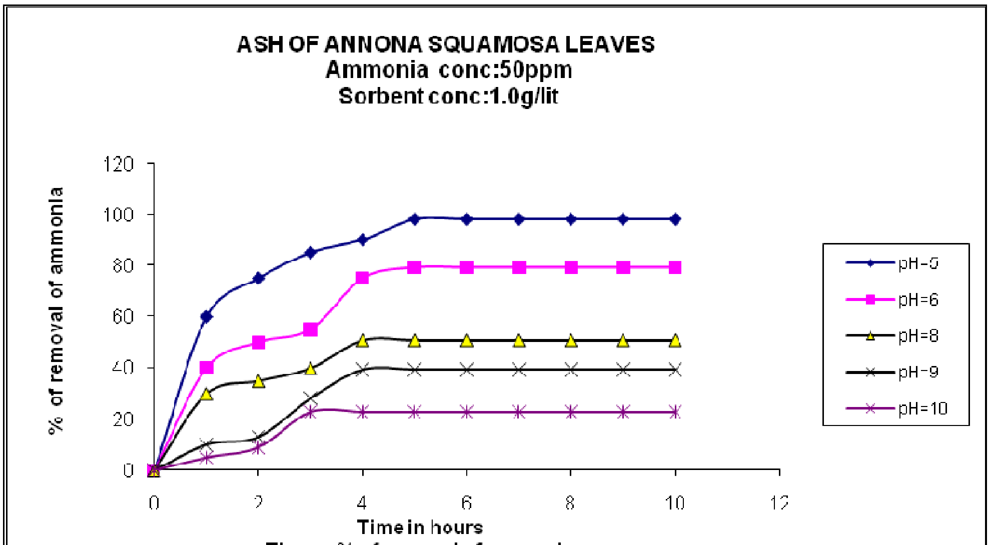
The extractions of Ammonia in presence of five fold excess of the common ions found in natural waters, namely Chloride, Fluoride, Sulphate, Phosphate, Carbonate, Calcium, Magnesium, Cupper and Zinc ions were studied with the successful adsorbents at optimum conditions of pH:5 , time of equilibration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

a. Cations namely, $Ca^{2+}$, $Cu^{2+}$, $Zn^{2+}$and $Mg^{2+}$ ions are interfering with the % of extraction of ammonia to some extent but in no case, % of extraction has come below 70.1%(vide Table No. 1)

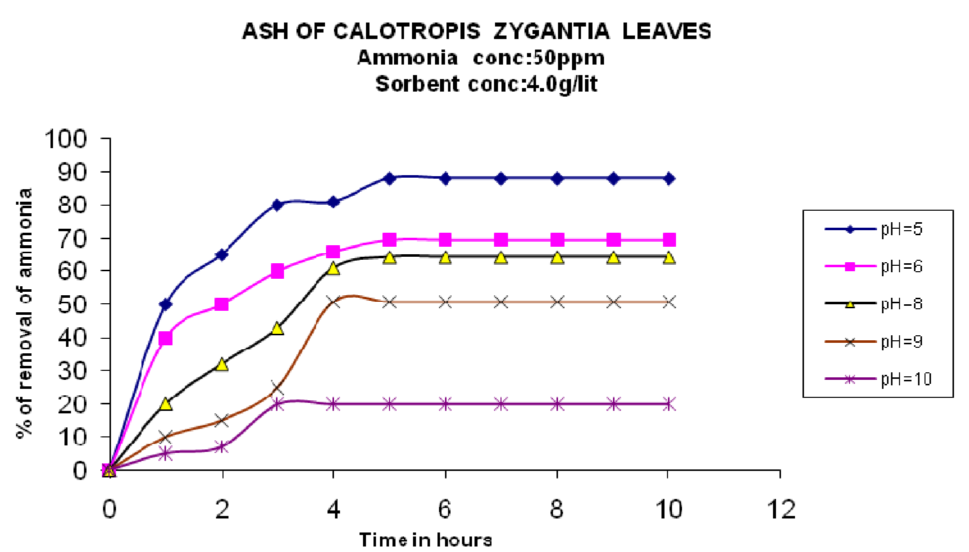
b. Anions of the present study viz., Chlorides, Fluorides, Sulphate, Phosphate and Carbonates are found to have marginal affect on the % of extractability of ammonia under optimum experimental conditions.



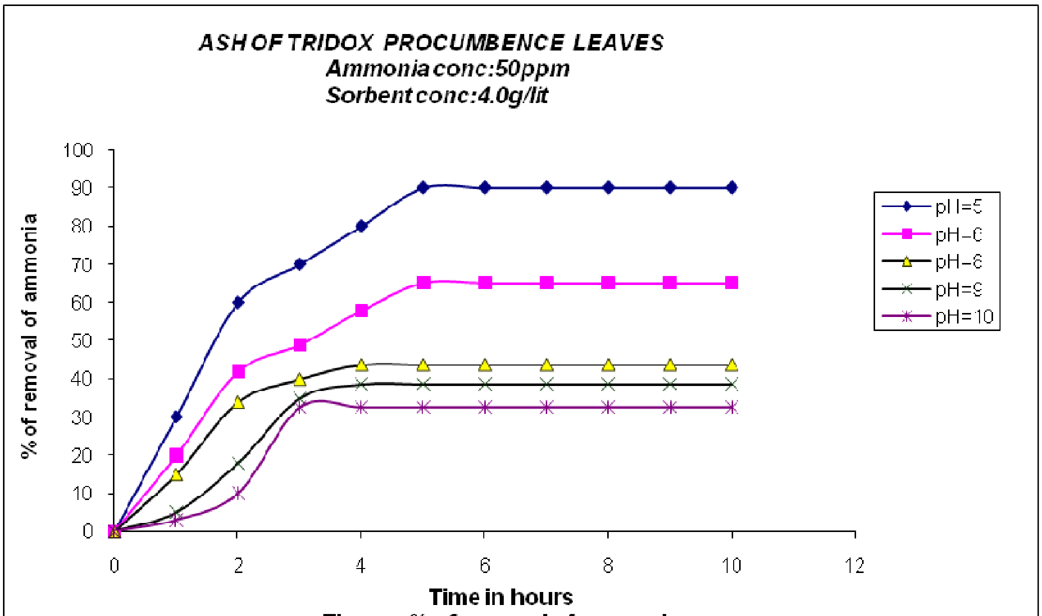
Time vs % of removal of ammonia
*Graph No: A-1*



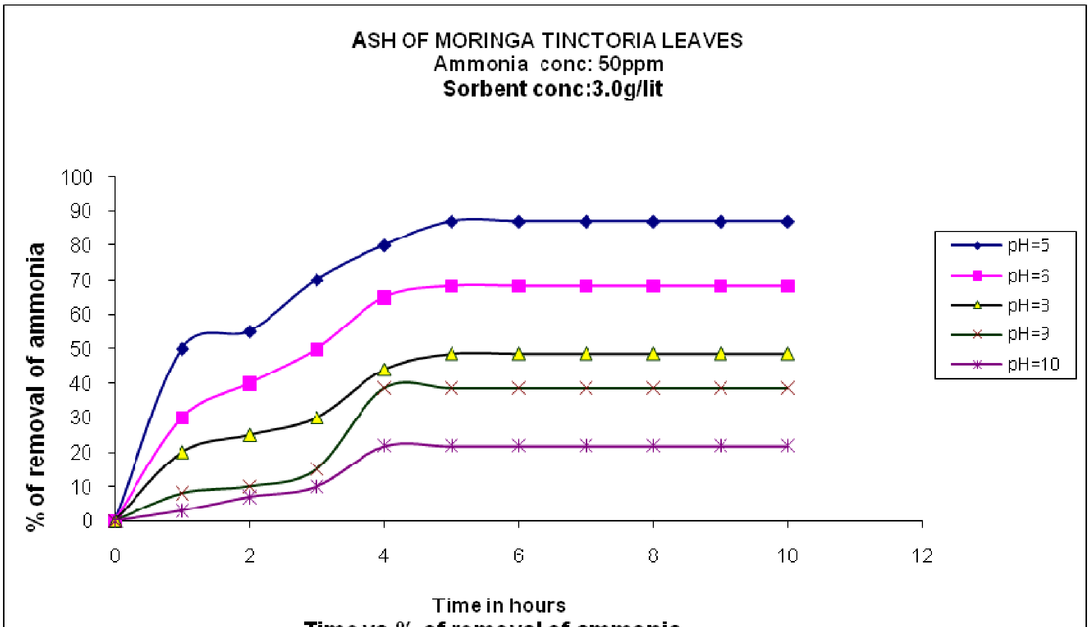
Time vs% of removal of ammonia
*Graph No:A-2*



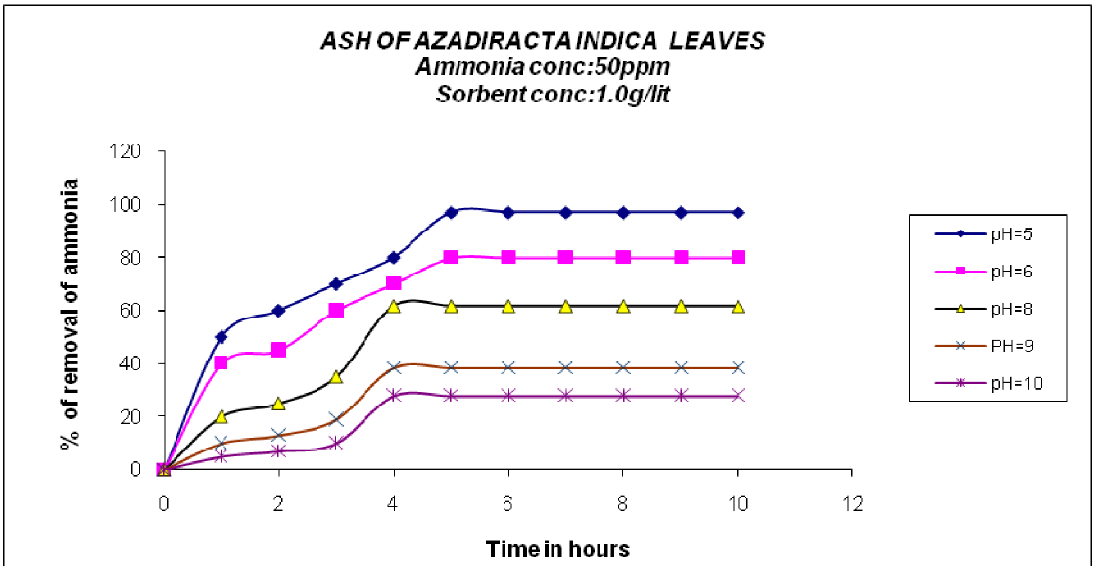
Time vs % of removal of ammonia
*Graph No:A-3*



Time vs % of removal of ammonia
*Graph No:A-4*

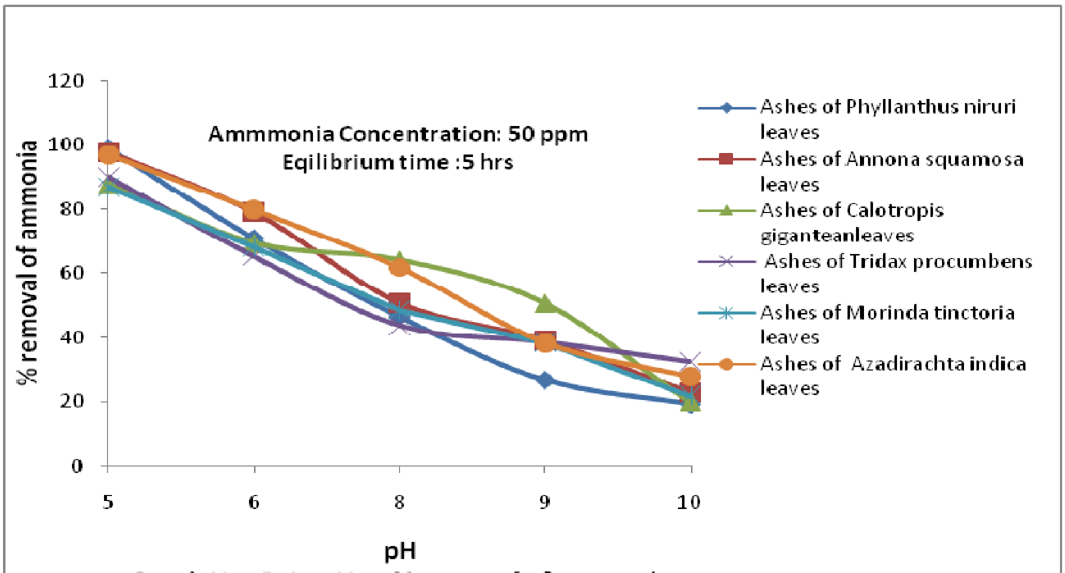


Time vs % of removal of ammonia
*Graph No:A-5*



Time vs % of removal of ammonia

*Graph No:A-6*



Graph No.:B:1: pH vs % removal of ammonia

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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.

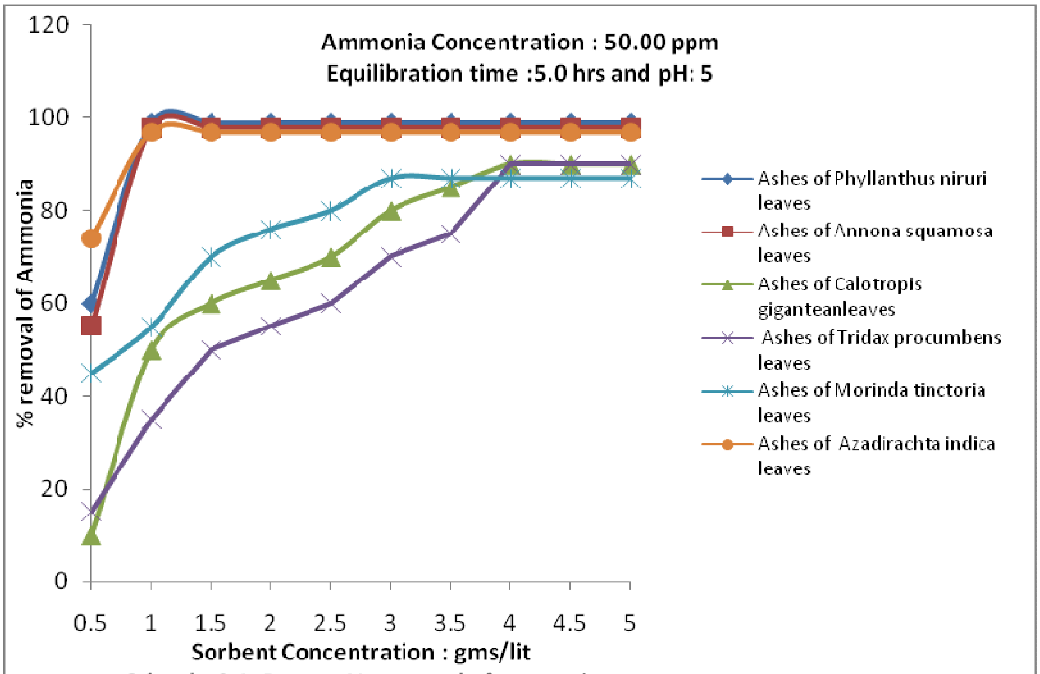
However, the sorption characteristics of the adsorbents for ammonia may be generally viewed as follows:

- Ammonia exists in aqueous solution either as ammonium ion ($NH_4^+$) or $NH_3$ depending on 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.

- Lingo celluloses like leaves and barks 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 of 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.

*Applications:*

The Applicability of the methodologies developed in this work were 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.*



Gdraph: C:1: Dosage Vs remotal of ammonia

| ***S. No.*** | ***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*** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $SO_4^{2-}$ | $NO_3^{2-}$ | $Cl^-$ | $PO_4^{3-}$ | $F^-$ | $CO_3^{2-}$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cu^{2+}$ | $Zn^{2+}$ | $Ni^{2+}$ |
| 1 | *Ashes of Phyllanthus niruri leaves:1.0 gms/lit* | 99.0%;<br>pH:5, 5.0hrs | 91.0 % | 92.2% | 91.2% | 87.3% | 90.3% | 90.4% | 79.6% | 81.0% | 78.8% | 81.3% | 83.0% |
| 2 | *Ashes of Annona squamosa leaves ;1.0gms/lit* | 98.0%<br>pH:5, 5.0 hrs | 91.1% | 90.1% | 92.0% | 90.1% | 92.2% | 90.5% | 82.1% | 82.0% | 78.0% | 76.3% | 81.0% |
| 3 | *Ashes of of Calotropis Zygantia leaves; 4.0 gms/lit* | 88.0%<br>pH:5., 5.0 hrs | 81.2% | 83.1% | 80.2% | 81.5% | 81.3% | 83.1% | 81.1% | 78.6% | 78.2% | 72.1% | 74.2% |
| 4 | *Ashes of Tridax procumbens leaves 4.0gms/lit* | 90.0%<br>pH:5, 5.0 hrs | 86.1% | 85.6% | 86.4% | 85.7% | 85.5% | 84.7% | 78.0% | 75.0% | 73.1% | 71.0% | 73.3% |
| 5 | *Ashes of Morinda tinctoria leaves; 34.0 gms/lit* | 87.0%<br>pH:5, 5.0 hrs | 83.0% | 82.0% | 83.6% | 84.4% | 85.2% | 82.4% | 70.1% | 73.1% | 72.0% | 70.2% | 72.5% |
| 6 | *Ashes of* Azadirachta indica *leaves;1.0 gm/lit* | 97.0%<br>pH:5, 5.0 hrs | 93.1% | 94.0% | 91.5% | 93.4% | 92.0% | 91.2% | 85.1% | 82.8% | 83.1% | 84.5% | 86.5% |

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

| **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 (18.5ppm) | Sample-6 (15.8ppm) |
| *Ashes of Leaves of Phyllanthus Niruri :at pH:5; Equilibration time:.5.0 hrs and sorbent concentration: 1.0 gms/lit* | 94.5 % | 93.2% | 91.3% | 95.1% | 96.7% | 92.4% |
| *Ashes of leaves of Annona squamosa . :at pH:5; Equilibration time: 5.0 hrs and sorbent concentration: 1.0 gm/lit* | 92.1% | 93.8% | 94.2% | 91.5% | 90.6% | 92.0% |
| *Ashes of Leaves of Calotropis Zygantia :at pH:5; Equilibration time: 5.0 hrs and sorbent concentration: 4.0 gms/lit* | 82.2% | 83.2% | 81.2% | 84.0% | 82.4% | 80.5% |
| *Ashes of Leaves of Tridax procumbens at pH:5; Equilibration time: 5.0 hrs and sorbent concentration: 4.0 gm/lit* | 85.6% | 86.7% | 84.5% | 85.6% | 85.6% | 84.9% |
| *Ashes of Leaves of Morinda tinctoria :at pH:5; Equilibration time: 5.0 hrs and sorbent concentration: 3.0 gms/lit* | 83.2% | 84.6% | 83.6% | 81.4% | 83.7% | 85.3% |
| *Ashes of Leaves of* Azadirachta indica *at pH:5; Equilibration time: 6.0 hrs and sorbent concentration: 1.0 gm/lit* | 90.2% | 92.5% | 91.4% | 93.1% | 92..0% | 91.0% |

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

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 as cited in the Table No. 2. % removal of Ammonia is found to be: *91.3 to 96.7% with ashes of leaves of Phyllanthus Niruri ; 90.6 to 94.2 % with the ashes of leaves of Annona squamosa ; 80.5 to 84.0% with Tridax procumbens leaves ashes ; 84.9 to 86.7% with the Morinda tinctoria leaves ashes and 81.4 to 85.3 % with* Azadirachta indica leaves ashes *and 90.2 to 93.1% with the ashes of leaves of Calotropis Zygantia .*

## CONCLUSION

- The importance of sorbents derived from bio-materials such as leaves in effecting the removal of ammonia in polluted waters has been explored.
- Ashes of leaves of *Phyllanthus Niruri , Annona squamosa , Calotropis Zygantia , Tridax procumbens, Morinda tinctoria and* Azadirachta indica are found to extract ammonia to an extent of 99.0%, 98.0%, 88.0%, 90.0%, 87.0% and 97.0% respectively at pH:5 , equilibration time of 5.0 hrs and at optimum sorbent concentrations.

- **Interference**:

Anions like Chlorides, Fluorides, Sulphate, Phosphate and Carbonates showed marginal interference while cations like $Ca^{2+}$, $Cu^{2+}$, $Zn^{2+}$and $Mg^{2+}$ interfered to some extent . However, the % of extractability of Ammonia never comes down 70.1%.

- The methodologies developed in this work with the different bio-sorbents are found to be remarkably successful when applied to real water samples collected from the effluents of industries and polluted lakes.

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