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The use of bio-adsorbents derived from *Cassia Auriculata, Celastrus Paniculata* and *Carmona Retusa* in the removal of ammonia from polluted waters

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ABSTRACT

Leaves and their ashes of Cassia auriculata, Celastrus paniculata and Carmona retusa are identified to have tendency of sorption towards Ammonia. Physico-chemical parameters such as pH, time of equilibration and sorbent concentration have been optimized for the maximum removal of Ammonia from polluted waters. More than 86.0% of Ammonia extraction is noted from simulated waters in all these sorbents at optimum conditions of extraction. Anions like Chlorides, Fluorides, Sulphate, Phosphate and Carbonates have marginal effect on the extraction while Cations like Ca^{2+}, Mg^{2+}, Cu^{2+}, $Zn^{2+}$and Ni^{2+} have interfered to some extent. The methodologies developed are successfully applied to samples collected from industrial effluents and naturally polluted lakes.

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

INTRODUCTION

The present research in developing pollution control methods indicates that the sorption nature of Biomasses and bio-wastes of flora or fauna origin are being successfully explored either in their native form or chemically modified form in controlling the polluting ions in waste waters [1-11]. These methods are proving to be potential alternatives to the classical and traditional methods of pollution prevention and are stimulating continuous and expanding research in this field [12-17].

Our research group is thriving in this aspect of pollution research and some successful eco-friendly methodologies have been developed [18-22]. While probing the biomaterials of different plants for their ability to control polluting ions, we noticed affinity between *Ammonia and adsorbents derived from Cassia auriculata, Celastrus paniculata and Carmona retusa*. Ammonia is a potential pollutant and its permissible limit as per European Association for drinking water is approximately 0.5 ppm and also a guide level is given as 0.05ppm [23-24]. The Ammonia is highly toxic due to its easy penetrating character through biological membranes and it causes headache, insomnia, nausea, diarrhea and a failure in glucose tolerance in animals and human beings [25-35]. Further, the ammonia accelerates “eutrophication” of lakes causing the depletion of D.O. content in water bodies and thereby causing the loss of aquatic life [36].

Researchers developed procedures based on Air stripping, ion exchange, and biological nitrification and de-nitrification. Clilnoptilolite zeolites are used in the control of ammonia [37]. Microwave radiation, natural clay minerals [38-42] and new concepts of microbial treatment processes have also been used in the removal of ammonia from polluted waters. The methods have one or the other disadvantage and a universally acceptable eco-friendly method is still eluding the researcher.

The present work is a thorough study on the optimization of extraction conditions such as pH, time of equilibration and sorbent concentration, for the removal of Ammonia from polluted waters using biomaterials derived from the leaves and their ashes of Cassia auriculata, Celastrus paniculata and Carmona retusa.

METIRIALS AND METHODS

All chemicals used were of analytical grade**.** 500 ppm stock solution of Ammonia was prepared and was suitably diluted as per the need. Nessler's reagent was prepared as per the literature.

A: Adsorbents:

Of the various bio-adsorbent derived from plants tried for the removal of Ammonia from synthetically prepared polluted waters by optimizing various physicochemical parameters such as pH, concentration of sorbent and time of equilibration, it has been observed that the leaves and their ashes of ***Cassia auriculata, Celastrus paniculata and Carmona retusa***, have affinity towards the Ammonia ions.

a: Cassia auriculata ***b: Celastrus paniculata*** ***c: Carmona retusa***

Fig No. 1: Plants found to have affinity towards Ammonia ions

Cassia auriculata is a branched perennial shrub belongs to Leguminosae family. It grows well in all regions of India even in dry stony regions. Its leaves, flowers and seeds have been found to have medicinal values and its bark is used in tanning of leather.

Celastrus paniculata is a straggling, twining and unarmed shrub with thin brown bark belonging to Celastraceae family. It is widely distributed predominantly in deciduous forests in India and is reported to have medicinal values. *Carmona retusa* is an evergreen shrub reaching 3-4 ft in height and it pertains to Boraginaceae family. It is common in dry scrub forests of Deccan Peninsula and Southern India. Its leaves are used medicinally to treat colic, cough, diarrhea and dysentery.

The leaves of *Cassia auriculata, Celastrus paniculata and Carmona retusa* were cut, washed with tap water, followed by distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: <75µ and activated at 105^{o}C in an oven and then employed in this study. Further, these plant materials were burnt to ashes which were also employed in this work.

B: Adsorption experiment:

Batch system of extraction procedure was adopted [43-45]. Carefully weighted quantities of adsorbents were taken into previously washed 1 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 vigorously in mechanical shakers and were allowed to be in equilibrium for the desired time. After the equilibration period, an aliquot of the sample was taken for Ammonia determination. Ammonia was determined Spectrophotometrically by using "Diphenyl Carbazide" method [46].

Estimation of Ammonia:

An aliquot amount of Ammonia sample was taken in a 50ml volumetric flask. To it 1ml of nessler's reagent was added successively and the solution was then diluted to the volume and mixed well. Then O.D. of the developed color was measured against blank at 525 nm using U.V. and Visible Spectrometer. Thus obtained O.D.value was referred to a standard graph (drawn between O.D and Concentration) prepared with known amounts of Ammonia by adopting the method of Least Squares to find concentration of Ammonia in unknown solutions.

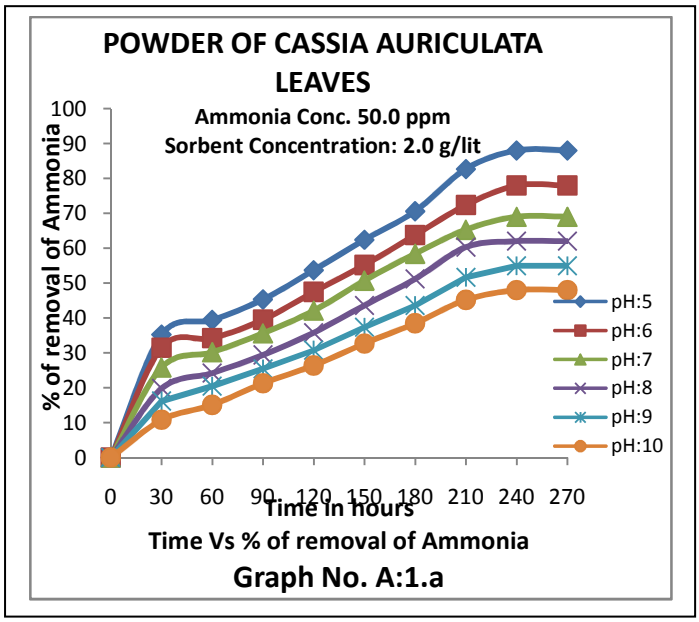
The sorption characteristics of the said adsorbents were studied with respect to the time of equilibration, pH and sorbent dosage. The results obtained were presented in the Graph Nos. A: 1-3; B: 1-3; C: 1-3.

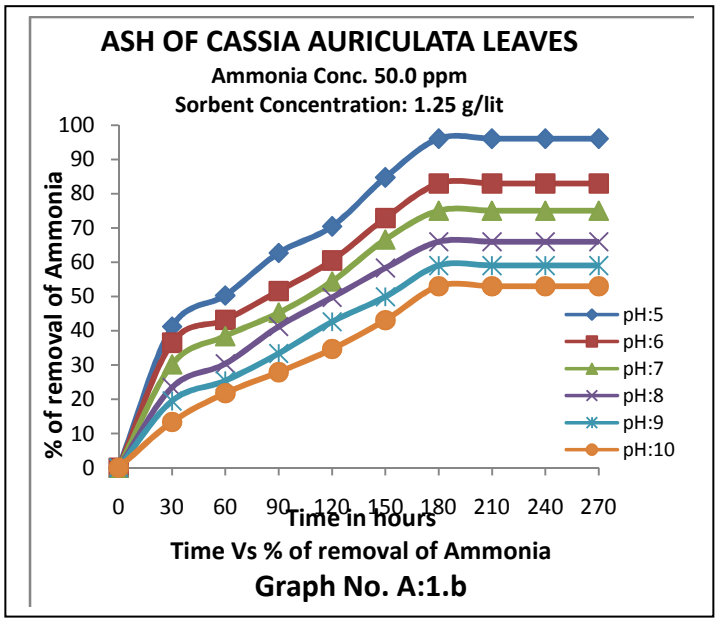
C: Effect of Interfering Ions:

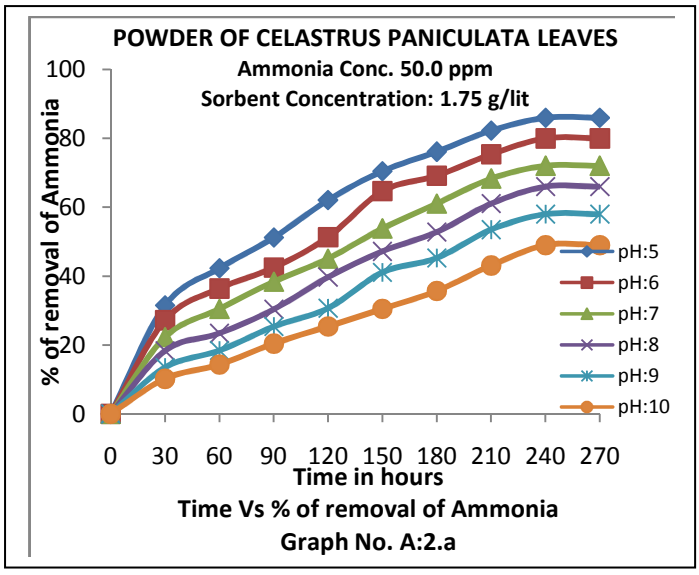
The synthetic mixtures of foreign ions and Ammonia were so made that the concentration of the former ions were maintained at fivefold excess than the latter. Then at optimum extraction conditions, Ammonia was extracted as per the procedure detailed above. Percentage of extraction was calculated and the results are presented in the Table No. 1.

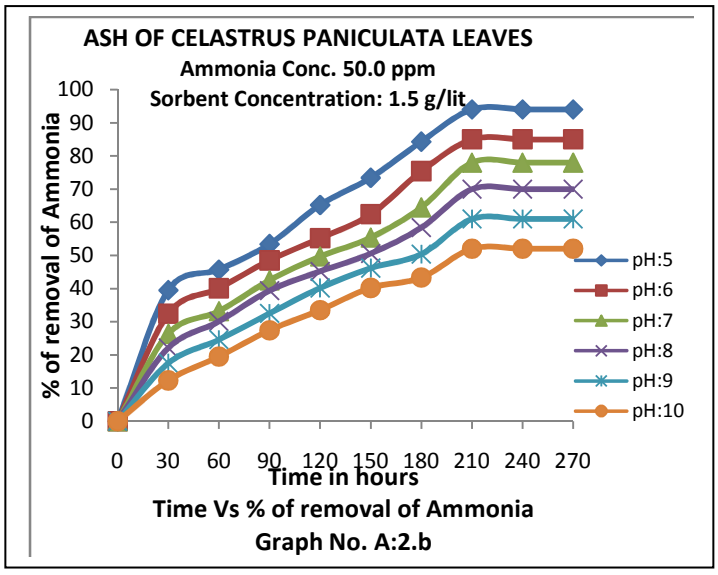
D: Applications:

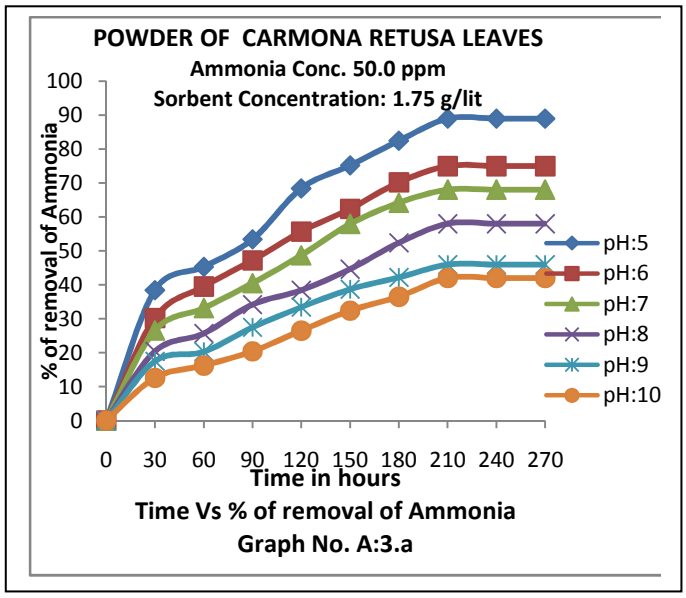
The procedures developed were applied to some real samples from industrial sewages and natural samples. *The results obtained were presented in the Table 2.*

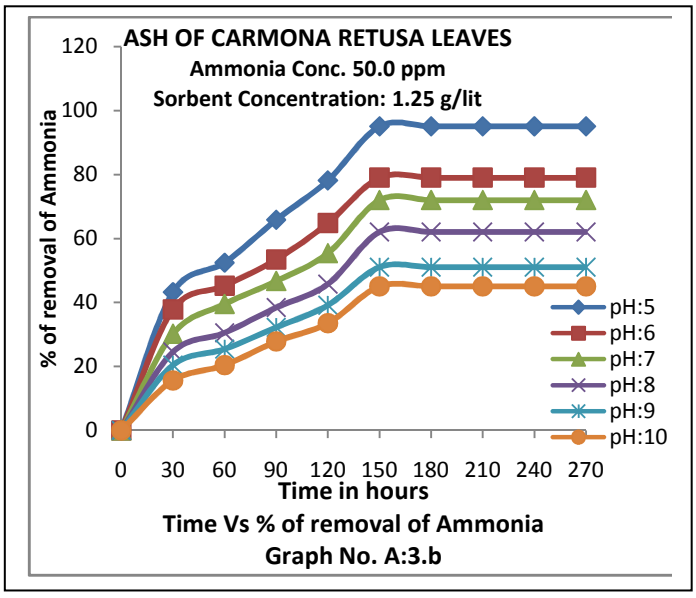


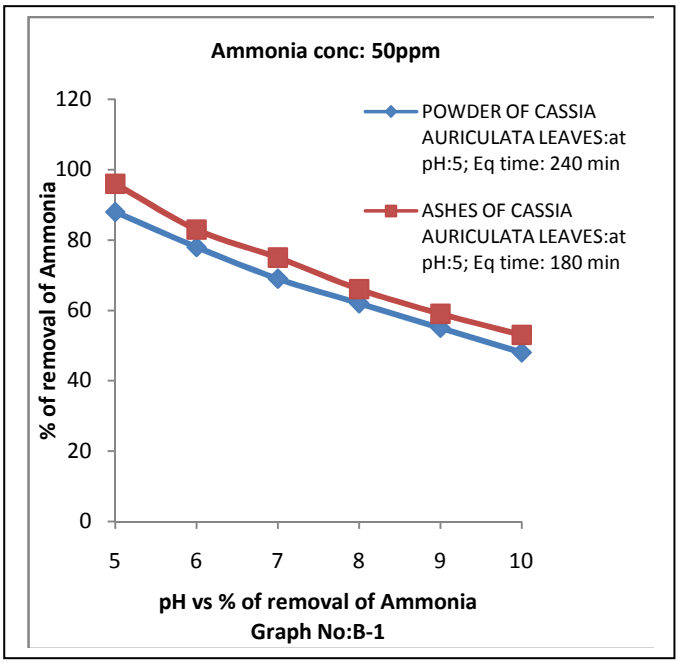


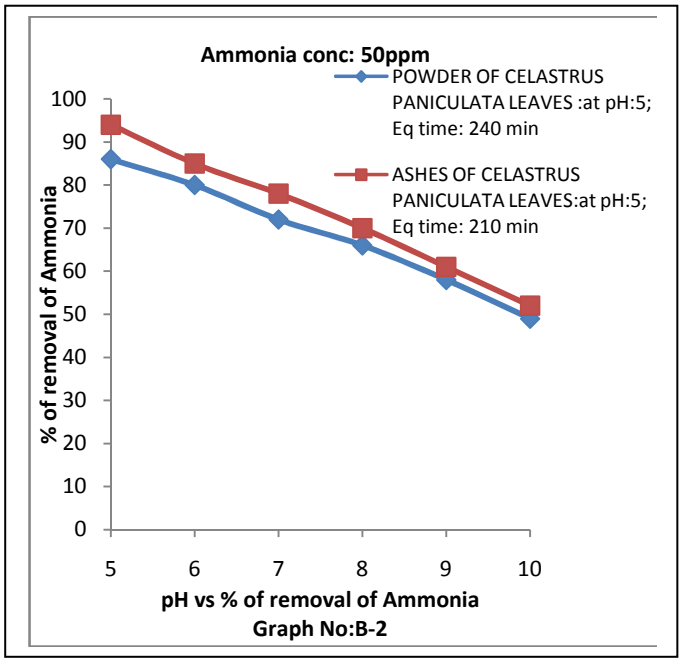


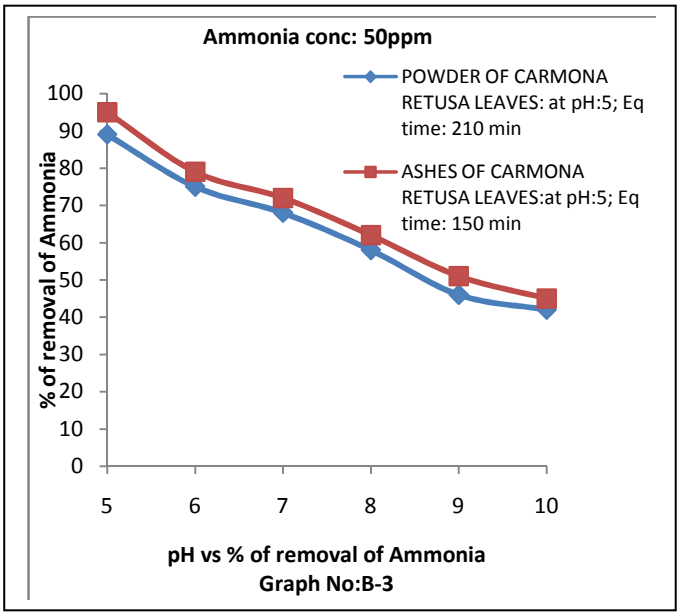


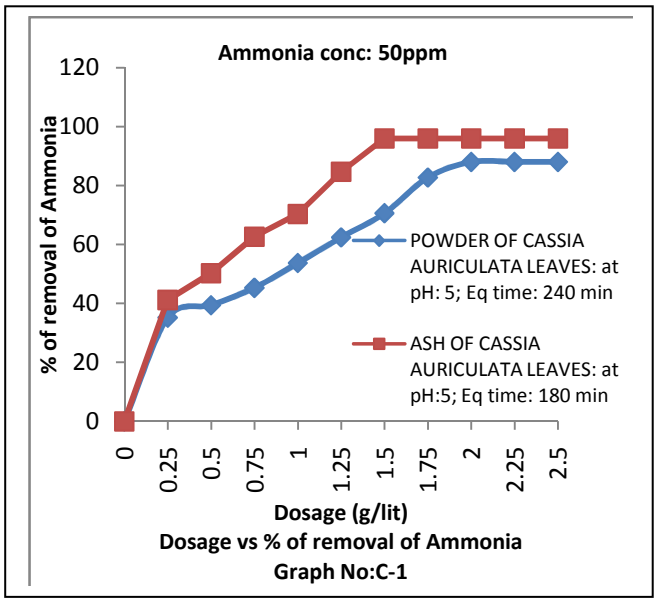

POWDER OF CARMONA RETUSA LEAVES
Ammonia Conc. 50.0 ppm
Sorbent Concentration: 1.75 g/lit
% of removal of Ammonia
Time in hours
pH:5
pH:6
pH:7
pH:8
pH:9
pH:10
Time Vs % of removal of Ammonia
Graph No. A:3.a

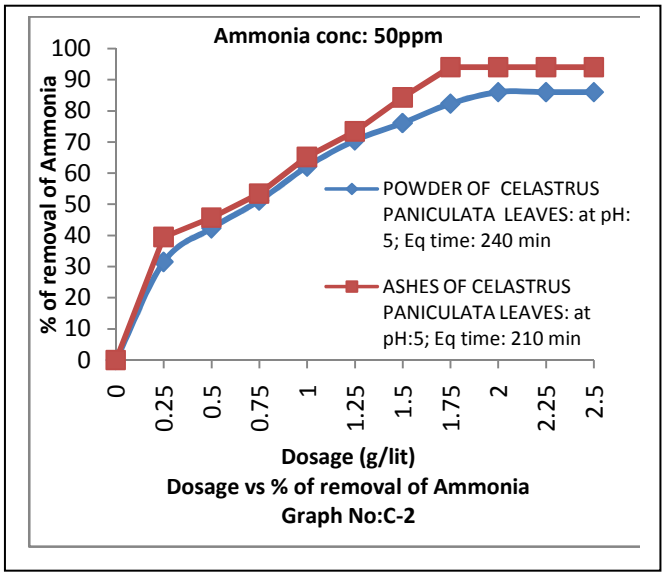

ASH OF CARMONA RETUSA LEAVES
Ammonia Conc. 50.0 ppm
Sorbent Concentration: 1.25 g/lit
% of removal of Ammonia
Time in hours
pH:5
pH:6
pH:7
pH:8
pH:9
pH:10
Time Vs % of removal of Ammonia
Graph No. A:3.b

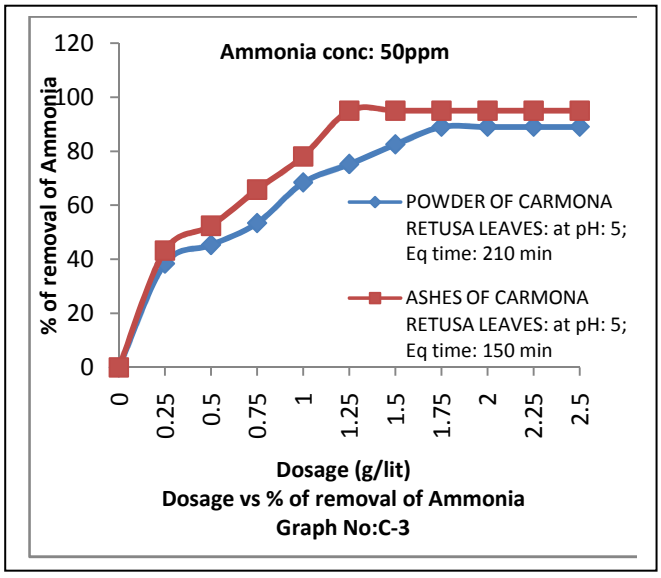

Ammonia conc: 50ppm
POWDER OF CASSIA AURICULATA LEAVES:at pH:5; Eq time: 240 min
ASHES OF CASSIA AURICULATA LEAVES:at pH:5; Eq time: 180 min
% of removal of Ammonia
pH vs % of removal of Ammonia
Graph No:B-1


Ammonia conc: 50ppm
POWDER OF CELASTRUS PANICULATA LEAVES :at pH:5; Eq time: 240 min
ASHES OF CELASTRUS PANICULATA LEAVES:at pH:5; Eq time: 210 min
% of removal of Ammonia
pH vs % of removal of Ammonia
Graph No:B-2


Ammonia conc: 50ppm
POWDER OF CARMONA RETUSA LEAVES: at pH:5; Eq time: 210 min
ASHES OF CARMONA RETUSA LEAVES:at pH:5; Eq time: 150 min
% of removal of Ammonia
pH vs % of removal of Ammonia
Graph No:B-3


Ammonia conc: 50ppm
POWDER OF CASSIA AURICULATA LEAVES: at pH: 5; Eq time: 240 min
ASH OF CASSIA AURICULATA LEAVES: at pH:5; Eq time: 180 min
% of removal of Ammonia
Dosage (g/lit)
Dosage vs % of removal of Ammonia
Graph No:C-1


Ammonia conc: 50ppm
POWDER OF CELASTRUS PANICULATA LEAVES: at pH: 5; Eq time: 240 min
ASHES OF CELASTRUS PANICULATA LEAVES: at pH:5; Eq time: 210 min
% of removal of Ammonia
Dosage (g/lit)
Dosage vs % of removal of Ammonia
Graph No:C-2


Ammonia conc: 50ppm
POWDER OF CARMONA RETUSA LEAVES: at pH: 5; Eq time: 210 min
ASHES OF CARMONA RETUSA LEAVES: at pH: 5; Eq time: 150 min
% of removal of Ammonia
Dosage (g/lit)
Dosage vs % of removal of Ammonia
Graph No:C-3

RESULTS AND DISCUSSION

The effects of various physicochemical parameters such as pH, time of equilibration and sorption concentration on the extraction of Ammonia have been presented in the Graph No. A: 1-3; B: 1-3; C: 1-3.

It can be inferred that the % of extraction is time and pH dependent. *With increase in time % of extraction increases at a fixed pH for a* fixed adsorbent and after certain time (varies from sorbent to sorbent), the extractability remains constant, i.e. an equilibrium state has been reached. In other words, there will not be any further adsorption after certain time of equilibration time (vide Graph Nos. A: 1-3). As for example, in the case of Cassia auriculata *leaves, at pH: 5, % of extraction is 35.2% at 30 min, 39.4% at 60 min , 45.3% at 90 min, 53.7% at 120 min, 62.4% at 150 min,70.6% at 180 min,82.7% at 210 min ,88.0% at 240 min and above.(vide Graph No.A:1.a).* The same trend is noticed in the case of other sorbents.

With *decrease* in pH, the % extraction is *increasing*. The optimum pH is found to 5 in all the sorbents of study (Vide Graph: B: 1-3). As for example, the powder of *Cassia auriculata* leaves extracts Ammonia up to 48.0 % at pH:10; 55.0% at pH:9; 62.0% at pH:8; 69.0% at pH:7, 78.0% at pH:6 and 88.0% at pH: 5 at an equilibrium period of 240 min, while the ash of *Cassia auriculata* leaves, extracts: 53.0 % at pH:10; 59.0% at pH:9; 66.0% at pH:8; 75.0% at pH:7, 83.0% at pH:6 and 96.0% at pH: 5 at an equilibrium period of 180 min. Similar trend is found in the case of other sorbents. At *pH:5, 6, 7, 8, 9 and 10 respectively,* extractability of Ammonia is found to be *86.0%, 80.0%, 72.0%, 66.0%, 58.0% and 49.0%* with the powders of *Celastrus paniculata* after an equilibration period of 240 min and *94.0%, 85.0%, 78.0%, 70.0%, 61.0% and 52.0%* with their *ashes* after an equilibration period of 210 min. The extractability is found to be *89.0%, 75.0%, 68.0%, 58.0%, 46.0% and 42.0%* with the powders of leaves of *Carmona retusa* and 95*.0%, 79.0%, 72.0%, 62.0%, 51.0% and 45.0%* with their ashes respectively at pHs *10,9, 8, 7,6 and 5*.

The maximum % of extractability is found to be marginally more with ashes of leaves than with raw powders of leaves. In most of the adsorbents, more than 86.0% extractability is observed at optimum conditions of pH, sorbent concentration and time of equilibration. *(vide Graph Nos. A: 1-3).*

The optimum *sorbent dosage* for maximum extraction Ammonias is found to be more in the case of leaves powder as compared to their ash, with *Cassia auriculata*, the optimum dosage is found to be respectively 2.0 gms/lit, 1.25 gms/lit with leaves powder and their ash; with *Celastrus paniculata*, 1.75 gm/lit, 1.5 gms/lit; with *Carmona retusa*, 1.75 gms/lit, 1.25 gms/lit (Vide Graph No.C:1-3).

The maximum percentage of extraction at optimum conditions of pH and sorbent dosage are found to be *88.0%, 86.0% and 89.0% with leave powders of Cassia auriculata, Celastrus paniculata and Carmona retusa and* 96.0%, 94.0% and 95.0% *with their ashes respectively (vide Graph Nos.A:1-3).*

Interfering Ions: The effect of fivefold excess of foreign ions on the extractability of Ammonia ions, has been studied and the results are presented *in Table No. 1.* Anions of the present study viz., Chlorides, Fluorides, Sulphate, Phosphate and Carbonates are found to marginally effect *and* Cations namely, Ca^{2+}, $Mg2^{+}$, $Cu2^{+}$, $Zn^{2+}$and $Ni2^{+}$ ions have interfered.

To understand the extraction characteristics, surface morphology of these bio-sorbents have to be taken into account. The functional groups present in these lingo celluloses' materials are either –OH-or -COOH groups. These groups dissociate at high pH values imparting negative charge to the surface and so electrostatic thrust for positively charged ions prevails on the surface at high pH conditions. But as the pH decreases, the dissociation of functional groups is not favored and further, protination occurs. This resulting positive charge at the interface, imparts thrust for anions at low pH condition. Below pH: 9.25, the predominant species of ammonia is NH_4^+ and above pH: 9.25, 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 1: Effect of Interfering Ions on the Extractability of Ammonia with different Bio-sorbents

S.No	Adsorbent and its Concentration	Maximum Extractability at optimum conditions	% removal of Ammonia in presence fivefold excess of interfering ions at optimum conditions: Conc. of Ammonia: 50ppm									
			SO_4^{2-}	NO_3^{2-}	Cl^-	$P0_4^{3-}$	F^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}
1	Powder of Cassia auriculata leaves 2.0 gm/lit	88.0% pH:5, 240 min	86.4%	83.1%	86.2%	87.2%	91.6%	89.2%	62.6%	64.7%	68.5%	69.5%	68.6%
2	Ash of Cassia auriculata leaves 1.25 gm/lit	96.0% pH:5, 180 min	88.3%	89..8%	92.0%	88.7%	93.2%	87.0%	63.6%	62.9%	61.3%	62.8%	60.0%
3	Powder of Celastrus paniculata leaves 1.75gm/lit	86.0% pH:5, 240 min	90.4%	96.2%	97.4%	91.9%	98.7%	98.1%	68.5%	66.5%	66.0%	67.0%	68.0%
4	Ash of Celastrus paniculata leaves 1.5gm/lit	94.0% pH:5, 210 min	92.5%	83.3%	86.4%	90.3%	92.6%	85.2%	63.0%	63.5%	65.5%	62.5%	61.0%
5	Powder of Carmona retusa leaves 1.75 gm/lit	89.0% pH:5, 210 min	88.4%	90.5%	82.3%	83.4%	95.1%	84.8%	65.5%	64.0%	63.3%	62.8%	67.0%
6	Ash of Carmona retusa leaves 1.25 gm/ lit	95.0 % pH:5, 150 min	88.2%	91.3%	91.8%	84.5%	97.3%	82.5%	70.0%	69.9%	68.7%	70.0%	69.1%

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: Sugar Factory effluents at Tadepalligudem in A.P. (21.5 ppm)	Sample:2: Dairy farm effluents in Guntur,A.P. (14.5 ppm)	Sample:3: Paper pulp Industry at Rajahmundry, A.P. (12.5 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 Cassia auriculata leaves:2.0 gm/lit	86.8 %	86.6%	84.2%	83.8%	82.4%	81.8%
Ash of Cassia auriculata leaves: 1.25 gm/lit	87.8%	86.9%	86.8%	87.1%	85.0%	84.5%
Powder of Celastrus paniculata leaves:1.75gm/lit	85.2%	84.7%	82.3%	85.4%	81.0%	82.1%
Ash of Celastrus paniculata leaves: 1.5gm/lit	89.7%	88.5%	84.4%	87.5%	82.9%	84.8%
Powder of Carmona retusa leaves: 1.75 gm/lit	88.1%	83.0%	79.5%	81.4%	82.7%	82.9%
Ash of Carmona retusa leaves: 1.25 gm/ lit	90.2%	88.6%	84.5%	85.6%	84.3%	85.9%

Applications

The procedures developed in this work have been applied for samples collected from the effluents of some industries and polluted lakes. The results obtained *have been presented in the Table No: 2*. It can be inferred that the procedures are remarkably successful.

CONCUSSION

1. Leaves and their ashes of *Cassia auriculata*, *Celastrus paniculata* and *Carmona retusa* have been found to be effective in the extraction of Ammonia *from polluted waters.*
2. Physicochemical parameters such as pH, time of equilibration and sorbent concentration have been optimized for the maximum removal of Ammonia.
3. More than 86.0% of Ammonia extraction is noted from simulated waters in all the sorbents of study at optimum conditions of extraction.
4. Fivefold excess of common foreign Cations namely, Ca^{2+}, $Mg2^{+}$, $Cu2^{+}$, $Zn^{2+}$and $Ni2^{+}$ ions have interfered and Anions of the present study viz., Chlorides, Fluorides, Sulphate, Phosphate and Carbonates has marginal effect on the extraction.
5. The procedures developed are successfully applied for some industrial samples.

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