

## Removal of Aluminium (III) from Polluted Waters Using Biosorbents Derived from *Achiranthus Aspera* and *Cassia Occidentalis*

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**Abstract:** Powders of leaves, stems and their ashes of *Achiranthus Aspera* and *Cassia Occidentalis* have been found to have a strong affinity towards Aluminum(III) in the pH range 4 and 8. The sorption abilities of these bio-products in controlling the Aluminum (III) pollution in waste waters have been studied with respect various physicochemical parameters such as pH, sorption concentration and equilibration time. Percentage of removal of Aluminum (III) is found to be pH sensitive and also depends on sorption concentrations and time of equilibration. Successful procedures are developed for the removal of Aluminum (III) to an extent of 100% from the synthetically prepared simulated waters using the bio-sorbents at extraction conditions of pH: 6-8, equilibration time: 120 minutes and at optimum sorbent concentrations. Cations even in tenfold excess have marginal interference with the extractability of Aluminum at the experimental conditions. Sulphate, Nitrate and Carbonate have marginal effect while the Fluoride and Chloride are markedly effect the % extraction; but phosphates are synergically enhancing the extractability of Aluminum (III) with some sorbents. The adoptability of the methodologies developed is tested with some real industrial effluents and polluted lake samples and found remarkably successful.

**Key words:** Aluminum (III) • Pollution control • Bio-sorbents • Applications

### INTRODUCTION

The consumption of elevated levels of Aluminum ions in drinking waters have been recognized hazardous to human health [1-6]. Aluminum is a neurotoxin and when it is ingested in the human system, it enters into the brain causing to dialysis encephalopathy syndrome and to Alzheimer's disease and also other neurodegenerative diseases. Further, it is reported that it causes toxicity in the bones and haematopoietic systems in humans [6]. Elevated levels of aluminum in waters are detrimental to fish dwelling and also for some birds whose diets are made up of insects from the shoreline of affected streams and lakes [7]. Concentrations exceeding 1.5 ppm constitute a toxicity hazard in the marine environment [8].

Because of toxicity of Aluminum ions, the maximum permissible limit in drinking waters is: 0.2 ppm as per WHO and US drinking water standards and 0.1 ppm in the countries like Canada and Sweden [8, 9].

The sources of aluminum contamination is attributed to the presence of 'residual aluminum' present in alum treated waters [10, 11, 12], effluents from aluminum based industries and also due to the salts of aluminum being added to many processed foods and medicine [13]. The other important source for aluminum contamination in natural water bodies is due to acid rains on the earth crust which has 8.1% of aluminum in abundance [6, 8]. The presence of aluminum in treated water is considered to be as an undesirable aspect of the treatment methods [10,14,15]. Thus there is a growing awareness throughout the Globe in developing suitable methods for the removal or control of aluminum in polluted waters.

Some procedures have been developed basing on the Cation exchange, reverse osmosis and electro-dialysis [16-19]. Treatment methods such as aeration/stripping, chemical oxidation, disinfection and anion exchange are ineffective. Processes such as coagulation, sedimentation and filtration (combined) as well as lime softening are

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moderately effective in Al removal [10]. Adil Denizli *et al.* [19] investigated the removal of aluminium by Alizarin Yellow-attached magnetic poly(2-hydroxyethylmethacrylate) beads. Ghazy S.E. *et al.* [20] worked on the kinetics of the removal of aluminum from water samples by adsorption onto powdered marble wastes.

Shaban El-Sayed Ghazy *et al.* [21] investigated the removal of aluminum from some water samples by sorptive-flotation using powdered modified activated carbon as a sorbent and oleic acid as surfactant adopting batch sorption methods. Javaweera M.W. *et al.* [22] studied the removal of aluminum by constructing wetlands with water hyacinth grown under different nutritional conditions. Septhum *et al.* [23] studied the adsorption Al (III) from aqueous solution onto Chitosan in a batch system. Mohamad Nasir Othman *et al.* [24] studied the aluminum removal by chelating ion exchange resin with Iontosorb (IO) and Polyhydroxamic acid (PHA).

Tony Sarvinder Singh, [25] have investigated the sorption of aluminum from drinking waters using a low-cost adsorbents. Rice husk char and activated rice husk char are prepared and characterized for various physicochemical properties. The performance of rice husk char (RHC) is compared with the other low-cost adsorbents for their aluminum removal capacity. The effect of different process conditions such as pH, initial sorbent/sorbate concentration and temperature on per cent aluminium removal have been investigated to ascertain the mechanism for aluminum adsorption. There is US patent pertaining to the removal of aluminum and sulphate ions from aqueous solutions [26].

*In the present work, the sorption characteristics of powders of leaves, stems and their ashes of different plants have been probed for their adsorption abilities towards Aluminum ions from polluted waters by optimizing the various physicochemical parameters such as pH, time of equilibration and sorbent concentrations.*

## MATERIALS AND METHODS

**Chemicals:** All chemicals used were of analytical grade.

**Stock Solution of Aluminium(III):** It was prepared by dissolving 1.319 gms of A.R. aluminum potassium sulphate in double distilled water and is made up to 1 lit. The resulting solution concentration was 75 ppm. It was suitably dilute as per the need.

**Buffer Solution: Concentrated:** 27.5 g of ammonium acetate and 11.0 g of hydrated sodium acetate were dissolved in 100 ml water and then 1.0 ml of glacial acetic acid was add and mixed well.

**Buffer Solution: Diluted:** To one volume of concentrated buffer solution, five volumes of distilled water was added and the pH of the solution was adjusted to 6.1 by adding solutions of Acetic acid or Sodium hydroxide.

**Eriochrome Cyanine R Solution:** 0.1 g of solid Eriochrome Cyanine R was dissolved in 100 ml of distilled water and filtered through a Whitman No. 541 filter paper. This solution was prepared daily.

**Hydrogen Peroxide Solution:** 5 volumes of H<sub>2</sub>O<sub>2</sub> Solution was prepared.

**Adsorbents:** Powders of leaves, stems and their ashes of various plants were tried for the removal of Aluminum from synthetically prepared polluted waters by optimizing various physicochemical parameters viz., pH, concentration of sorbent and time of equilibration. It has been observed that the sorbents derived from leaves and stems of Achiranthus Aspera and Cassia occidentalis have affinity towards the Aluminum (III) ions.



A: Achiranthus Aspera



B: Cassia Occidentalis

Fig. 1: Plants showing affinity towards Aluminum ions

*Achiranthus aspera* is commonly called as *Prickly Chaff Flower*, Devil's Horsewhip and in Sanskrit: as *Apamarga*. It belongs to the Amaranthaceous family and is distributed throughout the tropical world. This plant is used for many medicinal purposes, especially in obstetrics and gynecology, including abortion, induction of labor and cessation of postpartum bleeding. The Maasai people of Kenya use the plant medicinally to ease the symptoms of malaria.

*Cassia occidentalis* is an erect, foetid and annual herb belongs to Fabaceae family. It grows up to 60-150 cm in height and is found throughout in India. This herb is reported to be used as condiment and in perfumery. The young leaves are eaten as potherb or cooked along with unripe pods and eaten with rice; the leaf when eaten is reported to act as a prophylactic against leucorrhoea. The plant is used to cure sore eyes, haematuria, rheumatism, typhoid, asthma and disorders of haemoglobin and is also reported to cure leprosy. A decoction of the plant is used in hysteria, in dysentery and other stomach troubles and also as an application to sores, itch and inflammation of the rectum.

The leaves and stems of *Achiranthus Aspera* and *Cassia Occidentalis* were freshly cut from trees, washed with tap water, then with distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: > 75 microns and activated at 105°C in an oven and then employed in this study. Further these leaves and stems were burnt to ashes and these ashes were also used in this work.

**Adsorption Experiment:** *Batch system of extraction procedure was adopted* [27-29]. Carefully weighted quantities of adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500 ml/250 ml of Aluminum Potassium Sulphate 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 aluminum determination. Aluminum (III) was determined spectrophotometrically by using "Eriochrome cyanine R" method [8,30].

**Estimation of Aluminum(III):** An aliquot amount of Aluminum (III) solution was taken in a 250 ml beaker. To it 5 ml volume H<sub>2</sub>O<sub>2</sub> solution was added and mixed

well and the pH of the resulting solution was adjusted to 6.0 using either 0.2 M sodium hydroxide or 0.2 M hydrochloric acid with the help of pH-meter. At this stage 5 ml of Eriochrome cyanine R solution was added and mixed well. Then 50 ml of the dilute buffer solution was added and the solution was quantitatively transferred to a 100 ml volumetric flask with the help of distilled water and thus resulting solution was diluted to 100 ml. Thus obtained solution was well shaken to ensure thorough miscibility. Red to Pink color was developed depending on the concentration. After 30 minutes, the O.D. of the developed color was measured against blank at 535 nm using U.V. and visible spectrometer (Systronics make). Thus obtained O.D value was referred to standard graphs (drawn between O.D and concentration) prepared with known amounts of Aluminum by adopting method of Least Squares to find concentration of Aluminum (III) in unknown solutions. The sorption characteristics of the said adsorbents were studied with respect to time of equilibration, pH and sorbent dosage. At a fixed sorbent concentration, the % removal of Aluminum from sample waters was studied with respect to time of equilibration at various pH values. The results obtained were presented in the Graph Nos. A: 1-a to 1-d, A:2-a to 2-d and B: 1 & 2. To fix the minimum dosage needed for the maximum removal of the Aluminum ions for a particular sorbent at optimum pH and equilibration times, extraction studies were made by studying the % of extraction with respect to the sorbent dosage. The results obtained were presented in the Graph Nos. C: 1 & 2.

**Effect of Other Ions (Interfering Ions):** The interfering ions chosen for study were the common ions present in natural waters viz. Sulphate, Fluoride, Chloride, Nitrate, Phosphate, Carbonate, Calcium (II), Magnesium (II), Copper(II) Zinc(II) and Nickel (II). The synthetic mixtures of Aluminum and of the foreign ions were so made that the concentration of the foreign ion was maintained at tenfold excess than the Aluminum (III) concentrations as cited in the Table 1. 500ml of these solutions were taken in stopper bottles and then correctly weighted optimum quantities of the promising adsorbents (*as decided by the Graph Nos. A, B and C*) were added. Optimum pH was adjusted with dil. Hcl or dil. NaOH using pH meter. The samples were shaken in shaking machines for desired optimum periods and then small portions of the samples were taken out, filtered and analyzed for Aluminum (III). % of extraction was calculated from the data obtained. The results were presented in the Table 1.

Table 1: Effect of Interfering Ions on the Extractability of Aluminum (III) With Different Bio-sorbents

S.No	Adsorbent	Maximum extractability at optimum condition	% of Extractability of Aluminum (III) in the presence of tenfold excess of interfering ions at optimum extraction conditions										
			SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	F <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Ni <sup>2+</sup>
1.	Powder of Achiranthus Aspera leaves	100.0%,pH:6, 60 minutes, 2.5gm/lit	99.2%	100.0%	78.0%	100.0%	64.2%	99.0%	96.0%	99.5%	97.8%	99.2%	97.2%
2.	Powder of Cassia Occidentalis leaves	99.0%, pH:6, 120 minutes, 2.5gm/lit	98.3%	98.2%	71.2%	100.0%	63.2%	97.2%	95.1%	99.0%	97.1%	98.0%	95.6%
3.	Powder of Achiranthus Aspera stems	98.0%, pH:6, 120 minutes, 3.0gm/lit	97.6%	97.3%	70.2%	100.0%	63.1%	97.1%	94.8%	97.8%	96.2%	97.1%	95.6%
4.	Powder of Cassia Occidentalis stems	98.0%, pH:6, 120 minutes, 3.5gm/lit	97.4%	97.1%	70.1%	100.0%	62.1%	96.1%	94.0%	98.0%	96.0%	96.9%	94.9%
5.	Ash of Achiranthus Aspera leaves	100.0%, pH:6, 30 minutes, 2.0gm/lit	95.3%	95.8%	68.1%	100.0%	60.3%	94.2%	92.3%	95.5%	93.2%	94.1%	92.8%
6.	Ash of Cassia Occidentalis leaves	100.0%, pH:6, 90 minutes, 2.0 gm/lit	99.3%	100.0%	77.9%	100.0%	64.1%	98.9%	95.0%	99.4%	97.6%	98.9%	97.0%
7.	Ash of Achiranthus Aspera stems	98.0%, pH:6, 120 minutes, 2.5 gm/lit	95.3%	95.8%	68.2%	100.0%	60.3%	94.2%	92.3%	96.5%	94.2%	95.5%	93.7%
8.	Ash of Cassia Occidentalis stems	95.0%, pH:6, 120 minutes, 2.5gm/lit	94.4%	94.0%	64.1%	100.0%	60.1%	93.1%	90.1%	94.0%	93.0%	93.5%	91.0%

Table 2: Extractability of Aluminum (III) from Different Industrial Effluents and Natural Lake Samples using Bio-sorbents developed in this work

Samples Collected at Different Places	Conc. of Al(III) in the Sample	% of Maximum extractability							
		<i>Achiranthus Aspera</i>				<i>Cassia Occidentalis</i>			
		<i>Leaves Powders (mesh: &lt;75 μ) pH: 6; 60 min &amp; 2.5 gms/lit</i>	<i>Leaves Ashes pH: 6; 30 min &amp; 2.0 gms/lit</i>	<i>Stem Powders (mesh: &lt;75 μ) pH: 6; 120 min &amp; 3.0 gms/lit</i>	<i>Stem Ashes pH: 6; 120 min &amp; 2.5 gms/lit</i>	<i>Leaves Powders (mesh: 75 μ) pH: 6; 120 min &amp; 2.5 gms/lit</i>	<i>Leaves Ashes pH: 6; 90 min &amp; 2.0 gms/lit</i>	<i>Stem Powders (mesh: 75 μ) pH: 6; 120 min &amp; 3.5 gms/lit</i>	<i>Stem Ashes pH: 6; 120 min &amp; 2.5 gms/lit</i>
<b>Alum manufacturing Industrial effluents:</b>									
1	10.5 ppm	95.6%	89.3%	90.6%	92.3%	90.4%	95.3%	92.5%	90.5%
2	15.5 ppm	93.3%	87.1%	92.6%	86.6%	92.8%	91.6%	94.6%	92.5%
3	21.5 ppm	89.0%	94.2%	88.5%	88.5%	90.3%	93.1%	95.8%	94.5%
<b>Aluminum Sulphate manufacturing Industrial effluents:</b>									
1	14.5 ppm	89.3%	90.4%	93.5%	90.9%	88.9%	91.5%	90.5%	89.5%
2	16.5 ppm	85.1%	88.4%	90.3%	94.6%	91.1%	92.0%	93.5%	90.0%
3	18.8 ppm	90.8%	89.8%	91.5%	96.7%	92.6%	93.0%	94.5%	91.0%
<b>Natural polluted Lake Samples(fed with known amounts of Aluminum (III)):</b>									
1	10.0 ppm	95.1%	92.5%	90.3%	90.5%	93.4%	92.5%	91.5%	94.5%
2	20.0 ppm	93.9%	90.5%	94.5%	92.5%	91.3%	94.5%	94.5%	96.0%
3	25.0 ppm	91.9%	93.8%	93.0%	93.5%	90.2%	92.5%	95.5%	95.0%

**Applications of the Developed Bio-Sorbents:** The adoptability of the methodology developed with the new bio-sorbents derived from Achiranthus Aspera and Cassia Occidentalis plants in this work for removing Aluminum (III), is tried with some real sewage/effluent samples of some industries. For this purpose, three samples were collected from Alum manufacturing industries in Hyderabad and three from Aluminum sulphate manufacturing industries in Chennai and these samples were analyzed for the actual concentration of

Aluminium (III). Further, three more natural samples from three polluted lakes at different places in Bapatla mandalam of Guntur Dt of Andhra Pradesh were collected and these samples were fed with known amounts of Aluminum (III).

Then these samples were subjected to extraction for Aluminum (III) using the bio-sorbents developed in this work at optimum conditions of extraction. The results obtained were presented in the Table 2.

## RESULTS AND DISCUSSIONS

Leaves, stems and their ashes of *Achiranthus aspera* and *Cassia occidentalis* have been found to have affinity towards the Aluminum (III) ions. The extractability of Aluminum has been studied with respect to various physicochemical parameters such as pH, time of equilibration and sorption concentration and the results obtained are presented in the Graph No. A: 1-a to 1-d; A: 2-a to 2-d; B: 1&2; C: 1&2. The following observations are significant:

**Time of Equilibration:** Percent 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. In other words, there will not be any further adsorption after certain time of equilibration time (vide Graph Nos. A: 1-a to 1-d; 2-a to 2-d). As for example, in the case of *Achiranthus aspera* leaves powders as sorbents, the extractability of Aluminum is found to be 68% at 10 minutes, 71% at 20 minutes, 80% at 30 minutes, 89% at 60 minutes, 95% for 90 minutes, 100% at 120 minutes and above, at the optimum pH: 6-8 and sorption concentration: 2.5 gm/lit (vide Graph No: A: 1-a). The same trend is noticed in the case of other sorbents probed in this study.

**Effect of pH:** % of extraction is found to be *pH sensitive*. As pH increases, the % of extraction of Aluminium (III) is found to be increasing and is maximum in the range 4 to 8 and after pH: 8, the extractability is found to be decreasing (Vide Graph: B: 1 & 2). As for example, with the powders of *Achiranthus aspera* leaves, the % of maximum extractability is found to be 65% in 1.0N HCl; 75% in 0.5N HCl; 80% at pH: 1; 92% at pH: 2; 96% at pH: 4; 100% at pH: 6; 100% at pH: 8; 85% at pH: 10 after an equilibration time of 120 minutes and at sorption concentration of 2.5 gm/lit. With the ashes of leaves of *Achiranthus aspera*, the maximum extractability is found to be 75% in 1.0N HCl; 78% in 0.5N HCl; 85% at pH: 1; 94% at pH: 2; 96% at pH: 4; 100% at pH: 6; 100% at pH: 8; 88% only at pH: 10 after an equilibration time of 120 minutes and with sorption dosage of 2.0gm/lit. With stem powders of *Achiranthus aspera*, the maximum extractability is found to be 64% in 1.0N HCl; 74% in 0.5N HCl; 85% at pH: 1; 90% at pH: 2; 96% at pH: 4; 100% at pH: 6; 100% at pH: 8; 84% only at pH: 10 after an equilibration time of 150 minutes and with sorbent concentration of 3.0gm/lit. With stem ashes of *Achiranthus aspera*, the maximum extractability is found to be 65% in 1.0N HCl; 76% in 0.5N

HCl; 92% at pH: 1; 95% at pH: 2; 98% at pH: 4; 100% at pH: 6; 100% at pH: 8; 84% only at pH: 10 after an equilibration time of 150 minutes and with sorbent dosage 2.5gm/lit. Similarly in the case of *Cassia occidentalis* leaves, the maximum extractability has been found to be: 52% in 1.0N HCl; 62% in pH: 0.5N HCl; 75% at pH: 1; 85% at pH: 2; 90% at pH: 4; 100% at pH: 6; 100% at pH: 8 and decreased to 77% at pH: 10 after an equilibration period of 120 minutes with sorption concentration of 2.5gm/lit. With the ashes of leaves of *Cassia occidentalis*, the maximum extractability after 120 minutes is found to be 55% in 1.0N HCl; 65% in 0.5N HCl; 76% at pH: 1; 90% at pH: 2; 96% at pH: 4; 100% at pH: 6; 100% at pH: 8; and decreased to 82% at pH: 10, at sorbent concentration of 2.0gm/lit. With the stem powders of *Cassia occidentalis*, the maximum extractability has been found to be: 60% in 1.0 N HCl; 62% in 0.5NHCl; 72% at pH: 1; 80% at pH: 2; 92% at pH: 4; 98% at pH: 6; 100% at pH: 8 and decreased to 76% at pH: 10 after 120 minutes, with sorbent dosage of 3.5gm/lit. In the case of stem ashes of *Cassia occidentalis*, the maximum extractability has been found to be 65% in 1.0N HCl; 67% in 0.5NHCl; 78% at pH: 1; 90% at pH: 2; 94% at pH: 4; 100% at pH: 6; 100% at pH: 8; and decreased to 80% at pH: 10 after an equilibration period of 120 minutes, with the sorbent concentration of 2.5gm/lit.

- The maximum % of extractability is found to be more with ashes of leaves and stems than with the corresponding leaves and stem powders, at optimum conditions pH and sorbent concentration. (vide Graph Nos. A: 1-a to 1-d, 2-a to 2-d).
- In most of the sorbents, time of equilibration needed for maximum extractability of Aluminum is found to be less for ashes than with the raw powders of leaves and stems. The equilibration time needed for maximum extraction is found to be 60 minutes for the leaves powders of *Achiranthus aspera* while with their ashes, it is drastically reduced to 30 minutes. In the case of *Cassia Occidentalis* leaves powders, the optimum period of agitation is found to be 120 minutes while with their ashes, it is only 90 minutes. (vide Graph Nos. A: 1-2). It is interesting to note that in the most of the sorbents, more than 80.0% extraction especially in ashes, is noticed even at 20 minutes of agitation time.

**Sorbent Concentration:** The optimum sorbent dosage needed for maximum extractability of the Aluminum (III) is found to be more in the case of leaves and stem powders than with their ashes. Sorbent concentration for

maximum extraction at optimum conditions of pH and equilibration is found to be 2.5 gram/lit for the powders of leaves of *Achyranthus aspera* while with its ashes optimum sorption concentration is reduced to 2.0 gms/lit. In the case of powders of stems of *Achyranthus aspera*, the sorbent concentration is found to be 3.0gm/lit while with its ashes it is only 2.5 gm/lit. Similarly, with the powders of leaves of *Cassia Occidentalis* the optimum sorbent concentration is found to be 2.5gm/lit, while with its ashes 2.0 gm/lit. With the stem powders of *Cassia Occidentalis*, optimum sorbent dosage is found to be 3.5 gm/lit while with its ashes the optimum concentration is found to be 2.5 gm/lit. (Vide GraphNo.C:1 and 2).

- The % of maximum extractability of Aluminum(III) at optimum conditions of pH and equilibration time as given in Table 1, are found to be 100% with the leaves and stem powders and their ashes of *Achyranthus aspera* and *Cassia occidentalis* plants (vide Graph Nos.A:1-a to 1-d,2-a to 2-d).

**Interfering Ions:** The extractability of Aluminum ions in presence of tenfold excess of common ions found in natural waters, namely, Sulphate, Nitrate, Chloride, Phosphate, Fluoride, Carbonate, Calcium, Magnesium, Copper, Zinc and Nickel ions, has been studied. The results are presented in Table No. 1.

- *Cations* envisaged marginal effect on the % extractability of Aluminum (III) with the sorbents of the present work at the optimum conditions of time of equilibration, pH and sorbent concentration.
- *Anions like*  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  have least effected the % of extraction while Chlorides and Fluorides markedly effected the % of extraction. Phosphates synergistically increased the % of extraction. As for example with *Achiranthus aspera leaves powder*, the 100% extractability, at optimum conditions of pH and sorbent dosage, has been found to be marginally effected to 99.2%, 100% and 99.0% in presence of tenfold excess of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  respectively; but, Chlorides and fluorides markedly effected the extractability of Aluminum(III) from 100.0% to 78.0% and 64.2% respectively. With the bio-adsorbent: *Cassia occidentalis leaves powder*, % of extraction has been found to be marginally decreased from 99.0% to 98.3%, 98.2% and 97.2% in presence of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  respectively while the Chloride and fluoride decreased the % of extraction from 99.0% to 71.2% and 63.2% respectively and further,

the presence of phosphate enhanced the extraction from 99.0% to 100.0%. The same trend is found in the case of powders of stems and ashes of leaves /stems of *Achiranthus aspera* and *Cassia occidentalis*. For example with the ashes of leaves of *Achiranthus aspera* the maximum % of extractability of Aluminum has been found to be marginally decreased from 96.0% to 95.3%, 95.8% and 94.2% in presence of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  respectively while Chloride and Fluoride markedly decreasing the extractability to 68.1% and 60.3% respectively; the presence of Phosphate enhanced the extraction of Aluminum from 96.0% to 100.0%. In the case of ashes of leaves of *Cassia occidentalis*, % of extraction has been found to be effected from 100.0% to 99.3%, 100.0% and 98.9% in presence of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  respectively; markedly effected from 100.0% to 77.9% and 64.1% in presence of Chloride and Fluorides respectively; Phosphates synergized the % of extraction from 100% to 100%. Similarly, in the presence of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ , Chloride, fluoride and phosphate, the % of extraction has been found to be effected from 100.0% to 99.1%, 100.0%, 98.7%, 77.7% 63.9% and 100% respectively.

**Applications:** The Applicability of the methodologies developed in this work have been tested with respect to the real samples of diverse nature, collected from the sewages/effluents of aluminum based industries and also in natural polluted lakes. The results have been presented in the Table 2.

It is found that the sorbents developed in this work are successful in removing Aluminum (III) at optimum conditions of pH, equilibration time and sorbent dosage as cited in the Table No.2. Percentage of removal of Aluminum is found to be: 89.0% to 95.6% with leaves powder of *Achyranthus aspera* and 87.1% to 94.2% with their ashes; 88.9% to 93.4 % with leaves powder of *Cassia occidentalis* and 91.5% to 95.3% with their ashes; 88.5% to 94.5% with the stem powders of *Achyranthus aspera* and 86.6% to 96.7% with their ashes; 91.5% to 95.8% with the stem powder of *Cassia occidentalis* and 89.5% to 96.0% with their ashes.

## DISCUSSIONS

For a thorough understanding of the sorption mechanism of these bio-adsorbents, surface morphological studies using such modern instruments like X-ray Photo Electron Spectroscopy (XPS), Fourier

Transform Infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrum (EDS) in addition to the classical elemental chemical analysis before and after the sorption of the Aluminum (III) species on the sorbent surface, are needed. It is beyond the aims of this work.

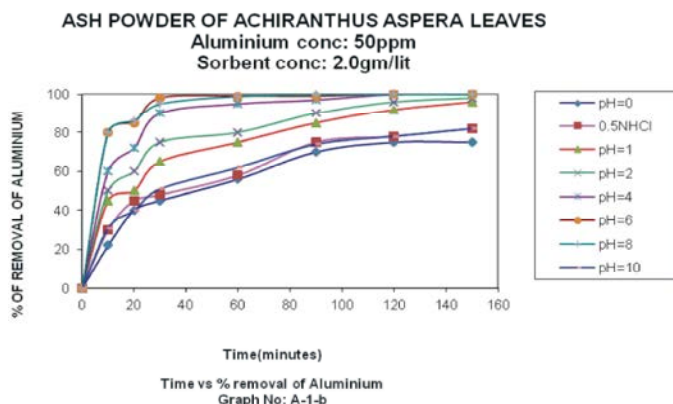
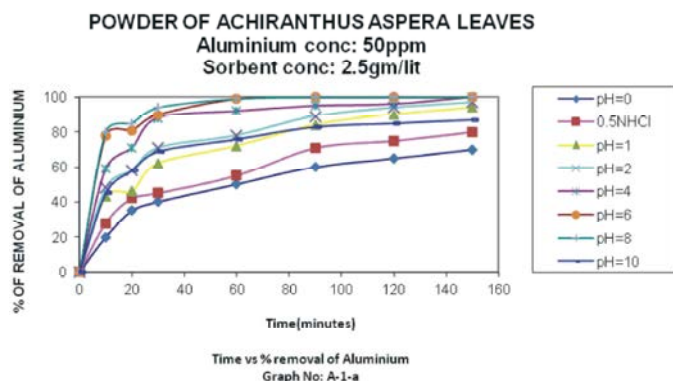
However, a rough nature of sorption characteristic may be accounted from the pH-dependent dissociation of surface functional groups namely -OH-or -COOH present in these biomaterials. At high pH values these groups dissociate importing negative charge to the surface and so the surfaces are surged with electrostatic thrust for positively charged ions. But as the pH decreases, the dissociation of functional groups is not favored and further, protonation occurs and nature of sorption is reversed. Hence, at low pHs, the surface positive charges develops affinity towards anions.

At low pH values (pH < 5), the main species for Aluminum (III) is  $Al[(H_2O)_6]^{3+}$ . However, as the pH increases,  $Al(OH)^{2+}$ ,  $Al(OH)_2^+$  are gradually formed and at neutral pH amorphous  $Al(OH)_3$  precipitates; at basic pH this precipitate dissolves to form  $Al(OH)_4^-$ . In the pH range 6 to 8, the Aluminum essentially exists as hydrated  $Al(OH)_3$  but it is not precipitated from dilute solutions of  $Al(OH)_2^+.(H_2O)_3$  in spite of insolubility, because the formation of  $Al(OH)_3$  is inhibited [30]. The bio-sorbents

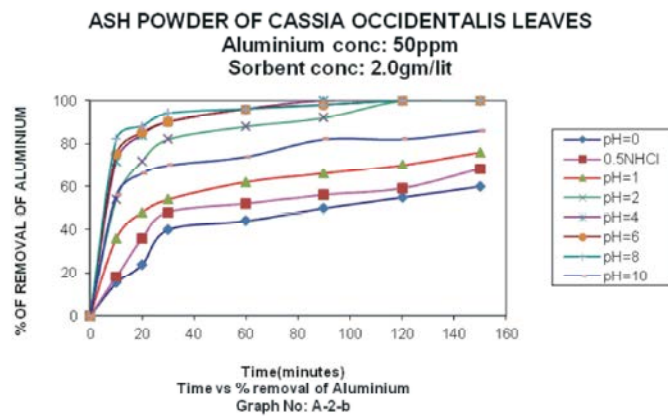
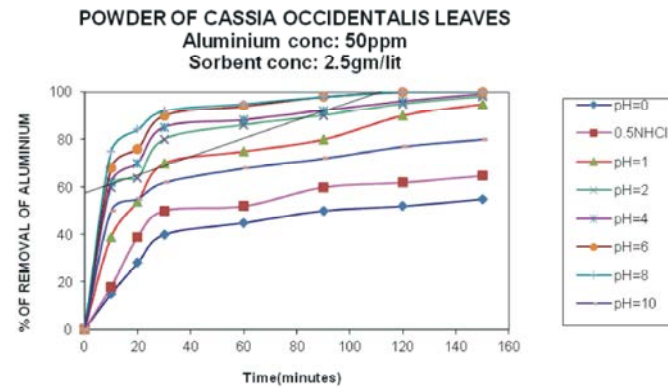
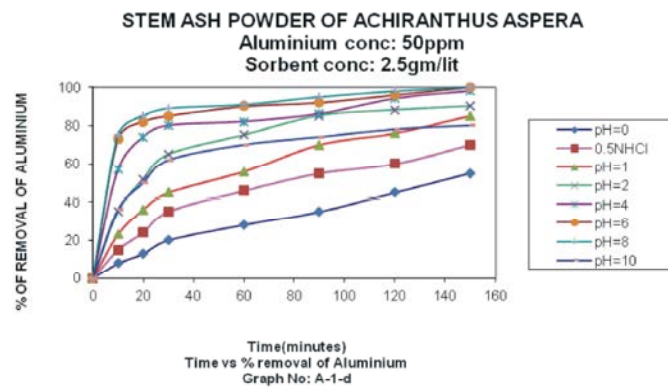
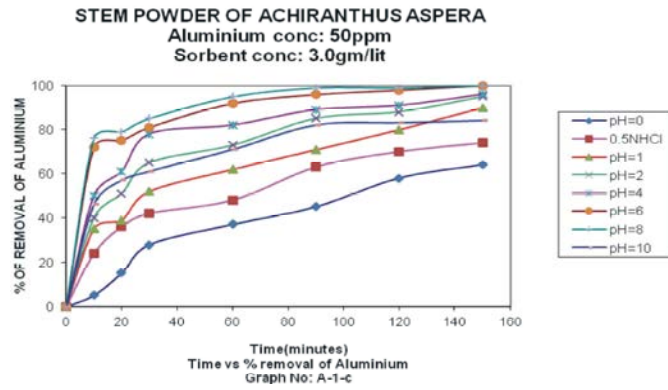
having functional groups OH/COOH bind the *hydrated* Aluminum hydroxide either due to electrostatic interactions or via hydrogen bonding resulting in the increase in the % of extraction. As the pH is increased to 10, the species exists is anion,  $Al(OH)_4^-$  [23,31] and is having less affinity towards the sorbent. Hence, % of extraction is decreased.

Ashes are the oxides of some heavy metals containing large amounts of silica. The ashes, contains '-OH' groups and '-O-'. The observed behaviors of extractability as pH varies may be understood in the same lines as described in the case of raw leaves or stem powders. In fact, in the literature it is reported that the silica possesses cation exchanging nature [32, 33, 34] and this supports the proposed logic for the observed behavior.

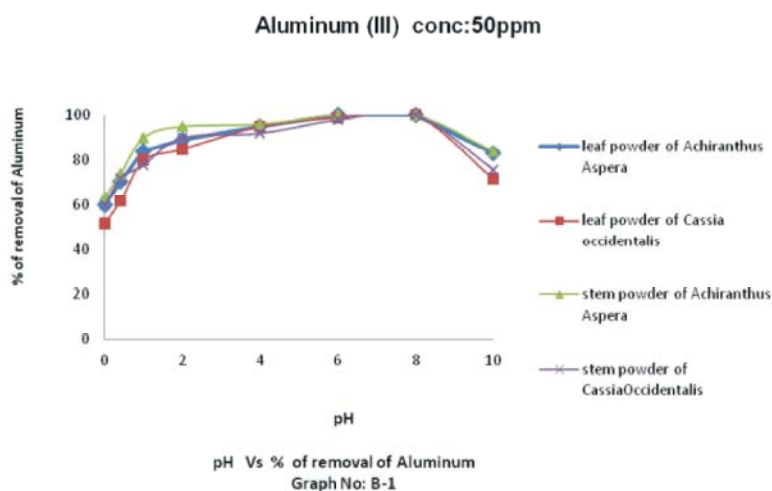
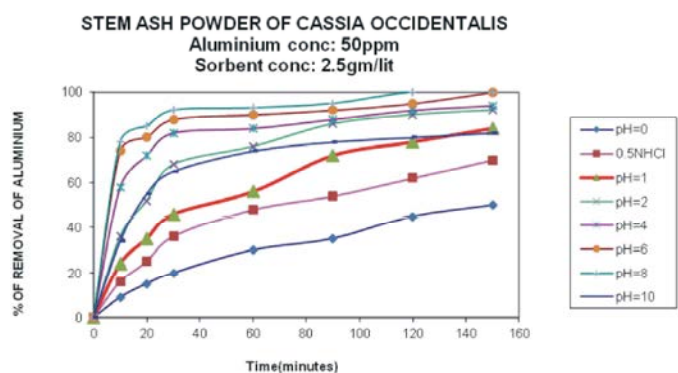
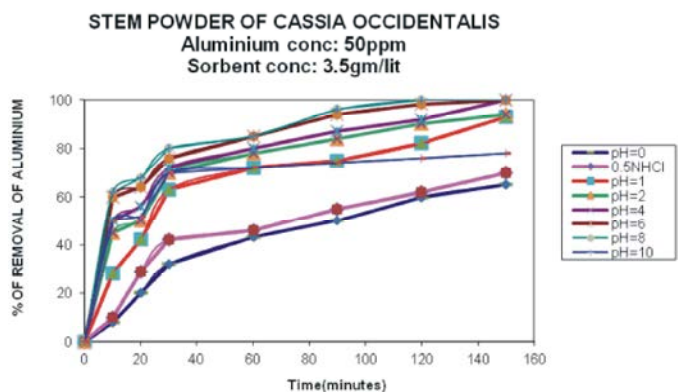
The decrease in the rate of adsorption with the progress in the equilibration time may be due to the more availability of adsorption sites initially and are progressively used up with time due to the formation of adsorbate film on the sites of adsorbent and finally resulting in the formation of pseudo-statical sorbent layers on the surface of sorbents and hence, the decrease in sorption capability of the adsorbent with the increase in the time.









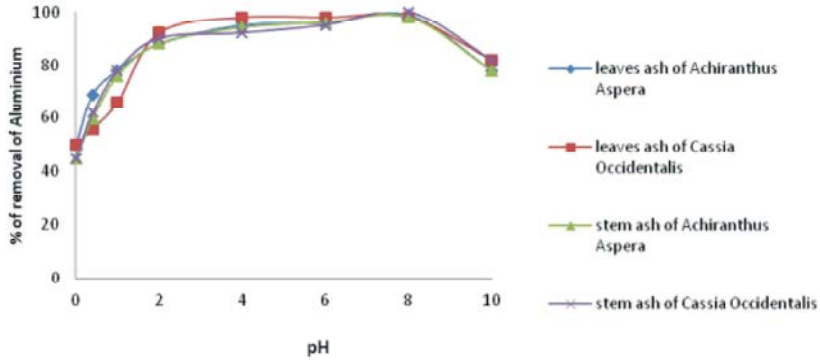


The observations made with respect to the interfering ions are interesting to note. Sulphate, nitrate and carbonate seldom affect the extractability of Aluminium (III) on adsorbents while chlorides and fluorides markedly decrease the extraction. This may be attributed to the fact that chlorides and fluorides desorb the Aluminium (III) from the adsorption sites of the sorbent (which are the weak cation exchange sites) by the formation of anionic complexes,  $AlF_4^-$  and  $AlCl_4^-$ . In presence of phosphate, the

% removal of Aluminium is enhanced and it may be due to the formation of sparingly soluble Aluminium Phosphate,  $AlPO_4$  which is gelatinous in nature and is trapped or occluded in the matrix of the sorbents and thus enhances the % of extractability of Aluminium (III) species.

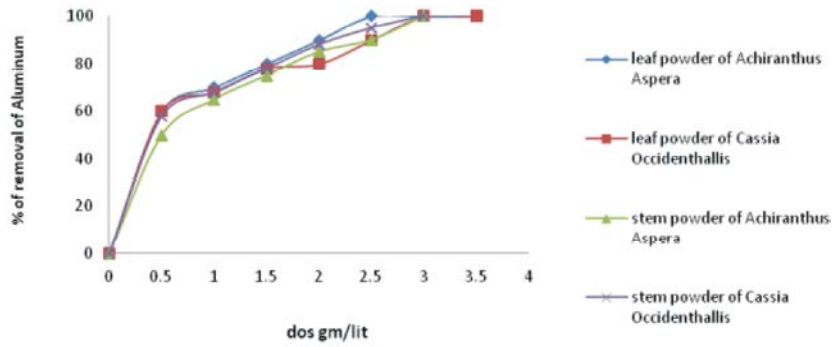
The extent of interference of the cations chosen for study viz.,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  on the extractability of Aluminium is minimal and further, when the % extractabilities are compared, they are as per the

**Aluminium (III) conc:50ppm**



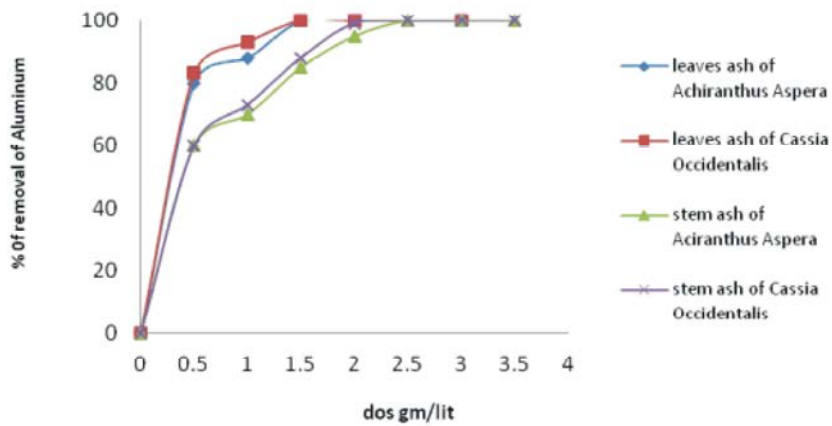
pH vs % of removal of Aluminium  
Graph No: B-2

**Aluminum (III) conc:50ppm**



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

**Aluminum (III)conc:50ppm**



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

well established cation exchange capabilities of the cations on the cation-exchangers viz.,:  $\text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}$  [35].

### CONCUSSIONS

- Bio-adsorbents derived from leaves and stems of *Achyranthus aspera* and *Cassia occidentalis* are found to be effective in the removal of Aluminium (III) species from waste waters at optimum conditions of pH(4-8), sorbent dosage and time of equilibration.
- Percentage of extraction of Aluminium (III) is found to be 100% with all the sorbents developed in this work from the synthetically prepared simulated waste waters at optimum conditions of pH: 6-8 (vide Graph No.A:1 &2), equilibration time and sorbent dosage as given in the Table 1.
- Most of the common cations, even at tenfold excess, envisaged marginal effect on the % of extraction of Aluminium (III) at optimum extraction conditions. *Anions like* Sulphate, nitrate and carbonate have least effected the % of extraction while chlorides and fluorides markedly effected the % of extraction. Phosphates synergistically increased the % of extraction.
- The procedures developed are successfully applied for some industrial and polluted lake samples.

### ACKNOWLEDGEMENT

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