New Bio-Sorbents in the Removal of Aluminium (III) from Polluted Waters

Anna Aruna Kumari[1], K. Ravindhranath[2]*
[1]Department of Chemistry, Acharya Nagarjuna University, Guntur-522510, A.P., India
[2]Dept of Chemistry, K L University, Vaddeswaram-522 502, Guntur Dt., A.P., India
***Corresponding author: E-Mail: ravindhranath.kunta@gmail.com**

ABSTRACT

The adsorption nature of bio-adsorbents obtained from *Pongamia pinnata* plant in the extraction of Al (III) ions from waste waters is studied by varying different parameters and by using Batch systems of extraction procedures. Various parameters have been optimized for the quantitative removal of Al (III) to an extent of 100%. Adsorption isotherms are analyzed and the obtained correlation coefficient (R^2) and dimensionless separation factor (R_L) values confirm that adsorption obeys Langmuir adsorption indicating monolayer formation. Further, the 'physisorption' nature of the sorption process is confirmed by Temkin as well as Dubinin-Radushkevich isotherms. On analysis of adsorption kinetics by various models, it is observed that pseudo second order model is better explaining the sorption process. The thermodynamic study reveals the endothermic nature for adsorption process. Common cations and some anions even in tenfold excess have shown marginal interference but Cl^- and F^- effected and while PO_4^{3-} synergistically maintained the 100% removal. The developed procedure is successful when applied to samples of waste waters from industries and contaminated lake waters.

KEY WORDS: Aluminum (III), pollution control, bio-sorbents, *Pongamia pinnata*, adsorption isotherms and kinetics, applications.

1. INTRODUCTION

Aluminum salts are widely used in different industries and also as coagulant in municipal water treatment (Yoshimum, 2004; Lindsay, 1996; Srinivasan, 1999; 2002). The industrial wastes are to be treated for the removal of Al (III) ions before disposing the waste to environment. If any lapse in this regard, leads to the contamination of water bodies with Al (III) ions. Further, the Aluminum present in the soils is leached into nearby water bodies (John Sorenson, 1996; Campbell, 2002) due to dwelling of human beings and their different activities. Thus accumulated Al (III) ions in water bodies are toxic and also effect the agricultural production (Flaten, 2001; Kochian, 1995). Further, the residual Aluminum in municipal waters is undesirable.

Epidemiological findings indicates that the Al (III) ions are neurotoxins (Flaten, 1996), harmful to fish (Miller, 1994; Campbell, 1983; Birchall, 1989), zooplankton (Haven, 1989; 1992), cyanobacteria (Pettersson, 1988), algae (Gensemer, 1991) and water weeds (Parker, 1989) and cause kidney problems, Parkinson and Alzheimer's disease (Flaten, 2001), bone softening (McClure, 1984), pulmonary fibrosis and anemia (Desccotes, 1988).

Because of hazardous nature of Al (III) ions (Flaten, 1996; Massey, 1989; Crapper, 1980), many countries imposed legislation and the allowed limit as per WHO is 0.2 ppm and as per Canada and Sweden, it is 0.12 (Lenore, 1998; Letterman, 1994). Hence, the researchers in environmental sciences are kindling their energies in removing Al (III) ions from industrial effluents or contaminated waters.

Cations exchange, precipitation, electro-dialysis and R.O methods have been investigated to address this problem (Pesavento, 1998; Matus, 2005; Singh, 2004) but these methods have one or other disadvantage and the universally acceptable simple, cheap and effective solution is eluding the researchers.

The bio-adsorbents prepared from plant materials either in their native or chemically modified state in controlling the polluting ions in waste waters, are supplementing or even replacing the traditional methods and this aspect is stimulating the research in this field (Paul, 1988; Denizli, 2003; Jekel, 1991; Ghazy, 2005; Shaban El-Sayed Ghazy, 2006; Tony Sarvinder Singh, 2006; Jawaweera, 2007; Septhum, 2007; Mohamad Nasir Othman, 2010). Our research group has been probing these aspects and developed methods for removing various polluting ions : Cr(VI) (Sekhar, 2012; Sree Devi, 2012; Hanumantha Rao, 2015; Naga Babu, 2016), Zn(II) (Papodu, 2014; Hanumantha Rao, 2015), Al (III) (Anna Aruna Kumari, 2012), F^- (Suneetha, 2014; 2015; Hanumantha Rao, 2012), NO_2^- (Suneetha, 2012; 2014), NO_3^{2-} (Suneetha, 2012), NH_3 (Prameela Rani, 2014; Suneetha, 2012), PO_4^{3-} (Divya Jyothi, 2012; Hanumantha Rao, 2015), Dyes (Srinivasa Reddy, 2012; 2014; 2015) and other metal ions (Shaik Karimulla, 2014), form waste waters.

The present investigation endeavors to probe the adsorbents prepared from the *Pongamia pinnata* plant in extracting Al (III) from waste waters.

2. MATERIALS AND METHODS

During our preliminary investigations, we notice affinity between Al (III) and *Pongamia pinnata* plant materials. *Pongamia pinnata*, is a medium-sized ever green shrub belonging to Fabaceae family and it grows well in alluvial soils. Various parts of the plant are used in folk lore curing different human ailments mainly pertains to abdominal and skin related problems. The leaves or stems cut from *Pongamia pinnata* were washed with distilled water and dried in Sun light. The dried materials were crushed and meshed to reduce the size of the particles below 75µ and activated at $105^{O}C$ using oven. Ash adsorbents were prepared by burning the leaves.

Adsorption Experiment: Batch systems of extraction procedures were adopted (Trivedy, 1979; Gerard Kiely, 1998; Metcalf and Eddy, 2003). Definite amounts of adsorbents were added to 250 ml of known concentrations of Al(III) taken in 500 ml stopper conical flasks and the pHs were adjusted to desired values and then the solutions were shaken in shaker for desired periods. Then the solutions were filtered and the content of Al (III) were estimated by "Eriochrome cyanine R" method as described elsewhere (Jeffery, 1989).

The adsorption natures of the adsorbents prepared were studied by gradually changing different physicochemical parameters. Using a constant adsorbent concentration, % removal of Al (III) from sample waters was explored by varying equilibration time at various pH values and the found results were depicted in Graph Nos: 1a to 1d, and 2.

Optimum dosage of adsorbent required for Al (III) removal was assessed by varying the dosage concentrations at fixed other optimum conditions of extraction and the results were shown in Graph No. 3.

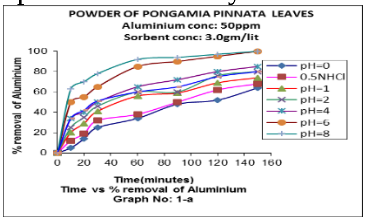
Effect of other Co-ions: The interfering ions chosen for study were the common ions naturally exist in waters viz. Sulphate, F^-, Cl^-, Nitrate, Phosphate, Carbonate, Ca (II), Mg (II), Cu (II), Zn (II) and Ni (II). The effect of tenfold excess of these ions on the % removal of Al (III) was studied and the results were noted in Table.4.

Applications: The procedures formed in this work were applied to samples collected from the effluents of Aluminum based industries at Hyderabad and also from polluted lakes at different places in Bapatla Mandalam of Guntur Dt. of Andhra Pradesh. Initially, the samples were analyzed for actual amounts Al (III) and then the Al (III) in the samples were extracted using the adsorbents developed in this work. The observations were given in Table.5.

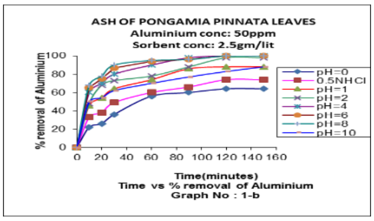
3. RESULTS AND DISCUSSIONS

The removal of Al (III) ions from waters was investigated by changing the various physicochemical parameters viz, pH, equilibration time, sorption concentration and effect of the temperature. Adsorption nature was analyzed using Freindlisch, Longmuir, Tempkin and DR models. Further, kinetics of adsorption was studied by correlating various kinetic models such as viz., Pseudo first and second order, Bangham's and Weber and Morris diffusion models, and Elovich equations. The results were presented in the Graphs and Tables at relevant places. The significant observations are:

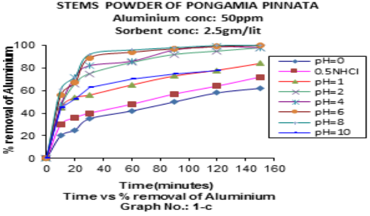
Time of equilibration: With the increase in the agitation time, % removal increases at constant pH and sorbent concentration. The removal comes to a study state after certain time. (Graph Nos. 1a to d). As for example, with the leaves powders of *Pongamia pinnata*, the extractability is : 50% at 10 minutes, 55 % at 20 minutes, 65% at 30 minutes, 85% at 60 minutes, 90% at 90 minutes, 95% at 120 minutes and100% at 150 minutes or above at an optimum pH:6 and at sorbent concentration of 3.0 gm/lit (vide Graph No.1a). The trend of adsorption is same with other sorbents probed in the study.



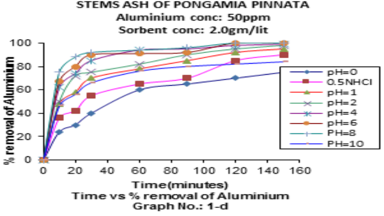
Graph.1a. Effect of equilibration time on % removal of Al (III) with leaves powder



Graph.1b. Effect of equilibration time on % removal of Al (III) with Leaves ash



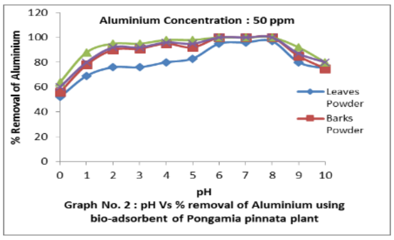
Graph.1c. Effect of equilibration time on % removal of Al (III) with stems powder



Graph.1d. Effect of equilibration time on % removal of Al (III) with stems ash

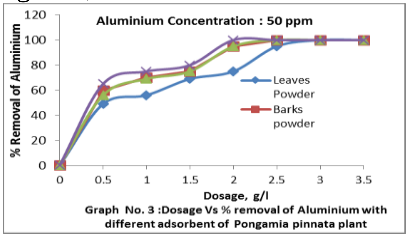
With the sorbents, agitation time needed for the maximum removal of Al (III) is less for ashes based adsorbents than with the leaves or stems based adsorbents. The optimum agitation time for maximum extraction is 150 minutes for the leaves and barks powders based adsorbent at optimum pH:6 while with their ashes the optimum equilibration times is 120 minutes (Graph Nos.1a to d).

Effect of pH: Adsorption is pH sensitive. The extraction is maximum when the solution pH is between 6 to 8 and below and above this range, the extraction falls (vide Graph No.2). As for example, with the leaves powder, the maximum removal is: 52% in 1.0N HCl; 62% in 0.5N HCl; 69% at pH: 1; 76% at pH: 2; 80% at pH: 4; 95% at pH: 6; 97% at pH: 8; and decreased to 75% at pH: 10 after an equilibration time of 150 minutes, and at sorption concentration of 3.0 gm/lit. With the leaves ash as adsorbent, the removal is: 64% in 1.0N HCl; 74% in 0.5N HCl; 88% at pH: 1; 95% at pH: 2; 98% at pH: 4; 100% at pH: 6; 100% at pH: 8; and decreased to 83% at pH: 10 after an equilibration time of 120 minutes and with sorption dosage of 2.5gm/lit. With stems powders, the maximum extractability is: 56% in 1.0N HCl; 64% in 0.5N HCl; 78% at pH: 1; 90% at pH: 2; 95% at pH: 4; 100% at pH: 6 &:8; and 75% only at pH: 10 after an equilibration time of 150minutes and with sorbent conc. of 2.5gm/lit. With the stems ash, the maximum extractability is: 60% in 1.0N HCl; 70% in 0.5N HCl; 80% at pH: 1; 92% at pH: 2; 96% at pH: 4; 100% at pH: 6 & 8 and 80% only at pH:10 after an equilibration time of 120 minutes and with sorbent dosage 2.0gm/lit.



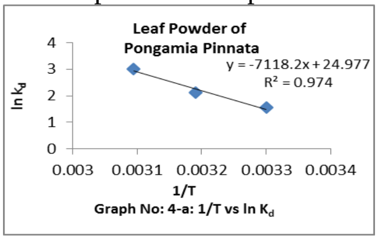
Graph.2. Effect of pH on % removal of Al(III)

Sorbent Concentration: The optimum sorbent concentration required for maximum extractability of the Al (III) is more with leaves and stem powders than with their ashes. Sorbent concentration for maximum extraction at optimum extraction conditions is 3.0 gram/lit for the leaves powder while 2.5 gm/lit with their ashes. With the stems powder the optimum sorbent concentration is: 2.5gm/lit, while with its ashes it is only: 2.0 gm/lit. (Graph No: 3).

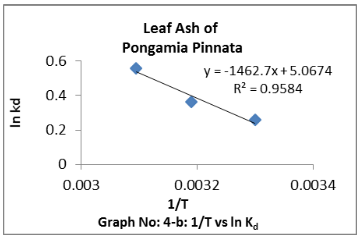


Graph.3. Effect of sorbent dosage on % removal of Al(III)

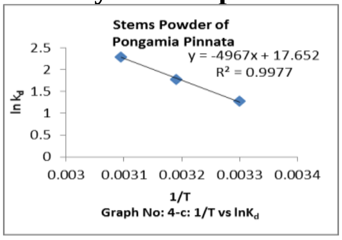
Effect of Temperature: The variation of solution temperature on the % removal of Al (III) was studied by conducting the extraction experiments at different temperatures 303, 313 and 323K and at optimum extraction conditions: pH: 6.0; contact time: 120 min; sorbent dosage: 3.0g/lit; concentration of Al (III) ion solution: 5.0 mg/lit . The results were depicted in Graph No.4 and Table.1.



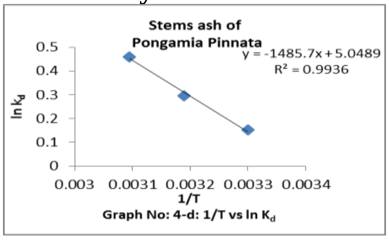
Graph.4a. Effect of Temperature on the extraction ability of leave powder



Graph.4b. Effect of Temperature on the extraction ability of leaves ash



Graph.4c. Effect of Temperature on the extraction ability of stems powder



Graph.4d. Effect of Temperature on the extraction ability of stems ash

Thermodynamic parameters namely, energy change (ΔG) (kJ/mole), change in enthalpy (ΔH) (kJ/mole) and change in entropy (ΔS) (J/K/mole) were determined at different temperatures by using the equations (Alagumuthu, 2010; Karthikeyan, 2007; Sekar, 2004). $\Delta G = -RT \ln K_d$; $\ln K_d = \Delta S/R - \Delta H/RT$; $K_d = q_e/C_e$ and $\Delta G = \Delta H - T\Delta S$ where K_d = the distribution coefficient for the adsorption, q_e = the amount of Al (III) ion adsorbed per liter of solution at equilibrium, C_e = the equilibrium conc. of Al (III) ion solution, T = absolute temp. R = gas constant. The values of ΔH and ΔS were calculated from the slope and intercept of a plot between ln K_d and 1/T and ΔG values were calculated from the equation $\Delta G = \Delta H - T\Delta S$ and tabulated in Table No. 1 (Horsfall, 2005; Viswanathan, 2010). It is observed that with rise in temp. from 303 to 323K (30 to 50^0C), the percentage removal of Aluminum(III) ion increases from 81.7% to 87.5% for leaf powders, 83.0% to 88.5% with Leaf ash, 92.6% to 97.2% with stems powder and 93.4% to 98.4% with stems ash.

Table.1. Thermodynamic parameters of Al (III) ions adsorption on different sorbents

Parameter	**ΔH(kJ/mol)**	**ΔS(J/mol/K)**	**ΔG (kJ/mol)**			**R²**
Temperature(K)			**303**	**313**	**323**	
Leaf Powder	59.180	207.6	-3.7228	-4.859	-7.8748	0.974
Leaf ash	12.16	42.13	-0.6053	-1.0266	-1.4479	0.9584
Bark Powder	41.295	146.75	-3.169	-4.6377	-6.105	0.9977
Bark ash	12.352	41.96	-0.3618	-0.7814	-1.201	0.9936

As the temp increases, the thickness of outer surface of the adsorbent decreases and kinetic energy of Al (III) ion increases and so, diffusion rate of Al (III) ion increases in the boundary layer and also into the internal pores of adsorbent. As is seen from the Table 1 that the positive values of ΔH indicates the physisorption and endothermic nature of adsorption (Bouberka, 2005).

The R^2 values close to one (0.974, 0.9584, 0.9977, 0.9366) for all the four adsorbents of *Pongamia pinnata* also indicate the endothermic nature of adsorption process. The positive ΔS values indicate the increase in disorder and randomness at the surface of adsorbents (Sairam Sundaram, 2009).

The negative values of ΔG reflect the spontaneity of adsorption process and in other words, the sorption forces are strong enough to cross the potential barrier at the boundary (Chaturvedi, 1988).

Adsorption Isotherms: Four well known adsorption isotherm models, Freundlich (1906), Langmuir (1919), Temkin (1940) and Dubinin-Radushkevich (1947) were selected to analyze the relation between the Al (III) conc. remaining in the bulk solution to the quantity of Al (III) adsorbed at the solid/solution interface at constant temperature.

Linear form of Freundlich equation is $\log (q_e) = \log k_f + (\frac{1}{n}) \log C_e$ and Linear form of Langmuir equation is: $C_e/q_e) = (a_L/k_L)C_e + 1/k_L$. According to Hall (1966), process of adsorption is unfavorable when the R_L is less than 1, linear when R_L is equal to 1and favorable when R_L is above 0 but below 1 and irreversible when R_L is equal to 0. Further this model is characterized by the dimensionless separation factor, $R_L = 1/ (1+ a_L C_i)$. The isothermal constants along with the correlation coefficient values calculated were given in Table 2.A.

R^2-values near to 1, indicate the validity of these two adsorption isotherms and confirm the heterogeneous surface of adsorbents and the monolayer coverage of Al (III) on the surface. The high correlation coefficient (R^2=0.9985, 0.9938, 0.9689 and 0.9983) values and dimensionless separation factor (R_L= 0.01594, 0.0142, 0.0212 and 0.01174) values in the range of 0-1, indicate the favorability of the Langmuir than Freundlich isotherm.

Table.2. A: Adsorption isothermal parameters of Freundlich and Langmuir plots for different adsorbents of *Pongamia pinnata* plant

S.No:	**Adsorption isotherms**	**Bio-sorbent**		**Slope**	**Intercept**	**R²**
1	Freundlich isotherms	Leaf Powder		0.223	0.9485	0.8868
		Leaf ash		0.2033	1.0761	0.8605
		Stems Powder		0.2123	1.0558	0.8591
		Stems ash		0.1453	1.2408	0.9087
			R_L	**Slope**	**Intercept**	**R²**
2	Langmuir isotherms	Leaf Powder	0.01594	0.0545	0.0341	0.9985
		Leaf ash	0.0142	0.0463	0.0259	0.9938
		Stems Powder	0.0212	0.0456	-0.0315	0.9689
		Stems ash	0.01174	0.0352	0.0219	0.9983

Table.2. B: Adsorption isothermal parameters of Temkin and Dubinin-Radushkevich plots for different adsorbents of *Pongamia pinnata* plant

S. No.		Adsorption isotherms characteristics			
1	**Temkin Isotherm**	**B**	**Slope**	**Intercept**	**R²**
	Leaf Powder	2.17778J/mol	2.1777	10.908	0.9041
	Leaf ash	2.4228J/mol	2.4228	14.254	0.9103
	Stems Powder	2.3586J/mol	2.3586	14.304	0.8684
	Stems ash	2.5554J/mol	2.5554	19.254	0.8954
2	**Dubinin-Radushkevich isotherm**	**E**	**Slope**		
	Leaf Powder	3.535KJ/mol	-4E-08	-7.075	0.8835
	Leaf ash	5.0KJ/mol	-2E-08	-7.024	0.8748
	Stems Powder	5.0KJ/mol	-4E-08	-7.1054	0.8942
	Stems ash	3.1622KJ/mol	-5E-08	-7.475	0.8825

Linear form of Temkin equation is $q_e = BlnC_e + BlnA$ where, RT/b = B (Hameed, 2009; Onyango, 2004) and Linear form of Dubinin-Radushkevich equation is $lnq_e = -\beta\varepsilon^2 + \ln q_m$, where $\varepsilon = RT \ln(1+1/Ce)$ (Monika, 2009). The isothermal constants along with the correlation coefficient values were evaluated and presented in Table 2.B. R^2-values are near to 1, reflect that these two adsorption isotherms are applicable to the present extraction systems and further confirm the heterogeneous surface of the adsorbent. For leaves, leaves ash, stems and stems ash, Temkin B values are 2.17778J/mol, 2.4228J/mol, 2.3586J/mol and 2.5554J/mol respectively and the Dubinin Radushkevich mean free energy, E =1v2ß, are 3.535 KJ/mol, 5.0KJ/mol, 5.0 KJ/mol and 3.1622 KJ/mol. As the E is less than 8 kJ/mol, it is an indication of 'physisorption' (Atkins, 1999) dominating the chemisorptions and ion exchange etc.

The "Physisorption" is nonspecific adsorption that occurs as a result of long range weak Vander Waals forces between Al (III) ions and adsorbent. As per Atkins (1999), characteristics for "physisorption" are the mean free energy (E) and also heats of sorption (B) values below 20kJ/mol. The B value of the present adsorbent system, further confirms the 'physisorption' nature.

Adsorption Kinetics: The rate of adsorption of Al(III) ion onto the different adsorbents were investigated using pseudo first-order model (Lagergren, 1898; Ho, 1999;2000) using the equation is $\log (q_e - q_t) = \log q_e - k_1 t/2.303$, pseudo second-order model (Ho, 1999; 2000) using $t/q_t = 1/k_2 q_e^2 - (1/q_e)\, t$, Weber and Morris intraparticle diffusion model (Weber, 1963) adopting $q_t = k_{ip} t^{1/2} + c$, Bangham's pore diffusion model(Aharoni, 1977) using $\log [\log (C_i/C_i - q_t m)] = \log (k_o/2.303V) + \alpha \log(t)$ and Elovich equations (Ozacar, 2005; Gerente, 2007) using $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$. From the plots of all these five kinetic models, various parameters were calculated and tabulated in Table.3.

Table.3. Kinetic parameters pertains to various adsorbents of *Pongamia pinnata* Plant

S.No:	Adsorption Kinetics			
1	**Pseudo first-order**	**Slope**	**Intercept**	**R²**
	Leaf Powder	-0.0097	0.8064	0.9802
	Leaf ash	-0.0134	0.7926	0.9881
	Bark Powder	-0.0091	0.7833	0.9882
	Bark ash	-0.0084	0.6968	0.9148
2	**Pseudo second-order**			
	Leaf Powder	0.0573	0.5179	0.9996
	Leaf ash	0.0489	0.2071	1.0
	Bark Powder	0.0489	0.1804	0.9996
	Bark ash	0.0394	0.1373	0.9998
3	**Weber-Mories Intra Particle Diffusion model**			
	Leaf Powder	0.4646	10.671	0.8751
	Leaf ash	0.3082	16.057	0.8518
	Bark Powder	0.3038	16.2	0.765
	Bark ash	0.3216	20.796	0.8658
4	**Bangham's pore diffusion**			
	Leaf Powder	0.6992	-1.3067	0.9262
	Leaf ash	0.6394	-1.0984	0.9768
	Bark Powder	0.7454	-1.275	0.940
	Bark ash	0.3293	-0.5759	0.953
5	**Elovich model**			
	Leaf Powder	1.989	6.466	0.960

	Leaf ash	1.332	13.21	0.952
	Bark Powder	3.249	3.304	0.981
	Bark ash	1.373	17.9	0.945

The applicability of the kinetic equations are compared using R^2. Of these five kinetic models, R^2 value for the pseudo second-order model is greater than other kinetic models and this indicates that the pseudo second-order model is the best fit to the observed data of the present studied adsorption systems. Of these models, the least is Weber and Morris diffusion model.

Interfering Ions: The % removal of Al (III) ions in presence of tenfold excess of co-ions found in waters, namely, SO_4^{2-}, NO_3^-, Cl^-, Phosphate, F^-, Carbonate, Ca(II), Mg(II), Cu(II), Zn(II) and Ni (II) ions, has been studied. The results tabulated in Table.4. Cations envisage marginal effect on the % extractability of Al (III) and it never comes down below 91.0%.

Anions like SO_4^{2-}, NO_3^- and CO_3^{2-} have least affected the % removal while Chlorides and Fluorides markedly affected. Phosphates synergistically maintained at 100% of extraction. Percentage of extractions ranges from 94.6 to 99.5% in the presence of Sulphates; 94.1 to 100% with Nitrates; 92.6 to 98.3% with Carbonates; 64.1 to 78.1% with Chlorides; and 60.1 to 68.8% with Fluorides at optimum extraction conditions as cited in the Table.4.

Table.4. Effect of Interfering Ions on the Extractability of Aluminum (III) using adsorbents pertaining to *Pongamia pinnata* plant

S. No	Adsorbent	Max. extraction at optimum conditions	% of Extractability of Aluminum (III) in the presence of tenfold excess of interfering ions at optimum extraction conditions										
			SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}	F^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}
1.	Leaves powder	100.0%, pH:6;150 minutes; 3.0gm/lit	94.6	94.1	64.1	100.0	60.1	92.6	91.3	94.3	93.2	94.0	91.4
2.	Leaves Ashes	100.0%; pH:6;120 minutes; 2.5gm/lit	99.3	100.0	78.1	100.0	64.3	99.0	96.1	99.6	97.9	99.3	97.3
3.	Stems powder	100.0%; pH:6;150 minutes; 2.5gm/lit	98.6	98.3	71.5	100.0	68.8	98.3	96.5	99.2	97.0	97.3	96.5
4.	Stems ash	100.0 % pH:6;120 minutes; 2.0 gm/lit	99.5	99.0	71.9	100.0	63.9	97.8	95.8	99.1	98.1	98.9	97.1

DISCUSSIONS

For a thorough understanding nature of mechanism of adsorption, morphological investigations using such modern instruments like XPS, FTIR, SEM and EDS in addition to traditional elemental chemical analysis with and without adsorbate onto the sorbent surface, are needed. It is beyond the nature of the present work. However, a rough nature of sorption characteristic may be accounted from the pH-dependent dissociation of functional groups ($–OH^-$ or –COOH) on the surface of these biomaterials.

At high pHs these groups dissociate imparting negative charge to the surface and so the surfaces are surged with electrostatic thrust for positively charged ions. But with decrease in pH, the dissociation of functional groups is less favored and further, protination may also occur and thereby, nature of sorption is reversed. Hence, at low pHs, the surface positive charges develop affinity towards anions. At pHs less than 5, the main species for Al (III) is Al $[(H_2O)_6]_3^+$. However, with increase in pH, $Al(OH)^{2+}$ are increasingly formed. In neutral pH, amorphous $Al(OH)_3$ precipitates while at high pHs, the precipitate dissolves to form $Al(OH)_4^-$. Between 6 to 8 pH , the Aluminum ions 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 as formation of $Al(OH)_3$ is inhibited (Albert Cotton, 1988).

The bio-sorbents through OH/COOH groups bind the hydrated Aluminum hydroxide either due to electrostatic interactions or via hydrogen bonding resulting in the increase in extraction. As the pH is increased to 10, the species exists is anion, $Al\ (OH)_4^-$ (Albert Cotton, 1988) and is having less affinity towards the sorbent. Hence, % removal 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 way as that of raw leaves or stem powders. In fact, the transitional pH for silica is 3 and at this pH value, the surface of silica changes from anion exchange nature to cation exchange nature and vice versa (Parks, 1965; Ravindhranath, 1987) 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. The observations made with respect to the interfering ions are interesting to note. Sulphate, nitrate and carbonate seldom affect the extractability of Aluminum (III) on adsorbents while chlorides and fluorides markedly decrease the extraction.

This may be attributed to the fact that chlorides and fluorides desorb the Aluminum (III) from the adsorption sites of the sorbent by the formation of anionic complexes, AlF_4^- and $AlCl_4^-$. In presence of phosphate, the % removal of Al (III) is enhanced and it may be due to the formation of sparingly soluble Aluminum 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 Aluminum (III) species.

Applications: The validity of procedures formed in this work were tested with respect to the real samples of diverse nature, collected from the sewages/effluents of Aluminum based industries and also in natural contaminated waters. Results were presented in Table.5.

It is inferred that the sorbents investigated are effective in the removal of Aluminum (III) at optimum extraction conditions as given in Table.5. The removal of Aluminum (III) is ranging from 91.5% to 98.2% with leaves powder and 91.5 to 96.5% with their ashes; 90.5% to 98.2% with the stems powder and 94.5% to 98.0% with their ashes.

Table.5. Applications: Extraction of Aluminum (III) from Different Industrial Effluents and Natural polluted Lake Samples using Bio-sorbents developed in this work

Samples Collected At Different Places	Conc. of Al(III) in the Sample	% of Maximum extraction of Al(III)			
		Pongamia pinnata			
		Leaves Powders (mesh:<75 µ) pH:6; 150 min& 3.0 g/l	**Leaves Ashes pH: 6; 120 min & 2.5 g/l**	**Barks Powders (mesh:<75 µ) pH:6;150 min & 2.5 g/l**	**Barks Ashes pH: 6; 120 min & 2.0 g/l**
Alum Industry effluents:					
1	10.0 ppm	93.5%	92.3%	90.5%	93.5%
2	14.0 ppm	92.8%	92.3%	91.0%	94.5%
3	16.5 ppm	91.5%	94.2%	92.1%	96.2%
Natural polluted Lake Samples (fed with known amounts of Aluminum (III)):					
1	7.5 ppm	97.8%	96.5%	97.6%	98.0%
2	10.5 ppm	98.2%	96.3%	96.7%	97.4%
3	11.5ppm	96.7%	95.8%	98.2%	96.9%

4. CONCLUSIONS

- Bio-adsorbents derived from leaves, or stems of *Pongamia pinnata* are investigated for the removal of Al (III) ions from polluted waters. Successful and effective methodologies have been developed.
- Percentage of removal of Al (III) is 100% with some adsorbents probed in the present investigation from the synthetically prepared simulated waste waters at optimum extraction conditions of pH: 6-8 (vide Graph No.1-a to 1-d), agitation time and sorbent conc. as given in the Table.4.
- Most of the common cations, even at tenfold excess, envisaged marginal effect on the removal of Al (III) at optimum extraction conditions. Anions like NO_3^-, SO_4^{2-}, and CO_3^{2-} have least affected the % removal while Cl^- and F^- markedly affected. Phosphates synergistically maintained the 100% removal.
- Freudlich and Langmuir isotherms are plotted and R^2 and R_L values are determined. These values have confirmed that adsorption obeys Langmuir adsorption indicating monolayer formation.
- On analysis of the nature of sorption process using Temkin and Dubinin-Radushkevich isotherms, 'physisorption' nature is revealed.
- Pseudo-first and second-order and also diffusion models such as Bangham's and Weber and Morris, have been used to understand the adsorption kinetics. Pseudo-second-order model is found to be suitable to explain the mode of kinetics.

- The thermodynamic study reveals the endothermic nature to the adsorption of Al (III) ions onto the surface and the adsorption increases with the rise in temperature.
- The procedures developed are successfully applied for some industrial and contaminated lake samples.

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