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EXTRACTION OF ALUMINUM (III) IONS FROM WASTE WATER USING AN ADSORBENT PREPARED FROM STEMS OF CASSIA *OCCIDENTALIS* PLANT

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ABSTRACT

Bio-materials pertaining to Cassia *Occidentalis* plant are investigated as an adsorbent for the removal of Al^{3+} ions from polluted water. By controlling extraction conditions namely, pH, adsorbent dosage, time of equilibration, rpm and temperature, 100% removal of Al (III) ions is achieved. Substantial amounts of Al^{3+} ions can be removed even at low pH values. Even tenfold excess of common co-cations and many of anions (except Cl^- and F^-) do not interfere in the extraction. Thermodynamic parameters are evaluated to know the nature of adsorption. The methodology developed is applied successfully for the removal of Al^{3+} ions from the industrial effluents and polluted water samples.

Keywords: Aluminum (III), Cassia *Occidentalis*, adsorption, applications

INTRODUCTION

The residual amounts of aluminum salts present in the effluents of various aluminum based industries are recognized as the mains source of aluminum pollution.[1,2] Further, the leaching of aluminum ions from the aluminum soils and alum-treated municipal water are also the other sources of contamination.[3,4] The consumption of Al (III) ions contaminated waters causes neurological disorders, Parkinson and Alzheimer's disease, anemia and orthopedic problems[5]. Further, the aquatic life such as fish, water weeds, algae, zooplankton etc is affected.[6,7]

Hence, the removal of Al (III) ions from waters assumes importance in pollution control investigations. The conventional methods based on precipitation are not effective at low concentrations while the methods based on ion-exchange, Reverse Osmosis, electro-dialysis are costly and not adoptable in large scale applications [8-10]. In this context, the use of bio-materials as adsorbents is an interesting aspect in view of availability, cheap and effectiveness. Investigations are made using HNO_3 activated carbons of olive stones (adsorbent) along with oleic acid (surfactant) for the removal of Al(III) ions [11]. Septhum et al (2007)[12] investigated the adsorption nature of Chitosan towards Al (III) from the water. Mexent ZUE MVE et al (2016) studied the removal of Al(III) ions using active carbon of Coula edulis Nut Shell[8]. Javaweera et al, 2007[13] investigated the extraction of Al (III) by growing water hyacinth in wetlands.

Adsorbents derived from the bio-materials of *Moryngea Millingtonia and Cygium Arjunum*[14], *Acacia Melanoxylon and Eichhornia Crassipes*[15] , *Ficus Racemosa*[1] and *Withania Somnifera*[16] plants are used for the extraction of Aluminum ions from waste water. Our research group is investigating these aspects of purification of polluted water and found some successful methods for the extraction of F^-, Pb^{2+}, Cr (VI), NO_2^-, NH_3, PO_4^{3-} and Dyes.[17-31]

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While we are investigating different bio-materials of the different plant as adsorbents for the extraction of different pollutive ions, stems of *Cassia Occidentalis* plant are noted to have good adsorption nature towards Al (III) ions. Hence, in this work, an adsorbent derived from *Cassia Occidentalis* plant stems is investigated for its adsorption nature towards Al (III) ions by optimizing the various conditions.

EXPERIMENTAL

Chemicals

All analytical grade chemicals were used and the solutions were prepared using double distilled water. Al^{3+} stock solution of concentration 100 mg/L was prepared and was diluted suitably as per the need. Buffer solutions (concentrated / diluted), Eriochrome cyanine R solution, H_2O_2 Solution (5 vol) were prepared as per the literature.

Adsorbent

Cassia occidentalis plant is an herbal plant and it belongs to *Fabaceae* family. It grows up to 60-150 cm in height and is found throughout in India. The stems of *Cassia Occidentalis* were cut to pieces and were thoroughly washed with distilled water. Then they were dried in sunlight and dried material was crushed to <75 microns. Thus obtained powdered material was activated at 105° C for 1 h in an oven and stored in an air-tight bottle. It used as an adsorbent in this investigation. Thus obtained *Cassia Occidentalis* Stems powder is named as COSP.

Fig.-1: *Cassia Occidentalis* Plant having an Affinity towards Al(III) Ions

Adsorption Experiment

Batch procedures were adopted [28,32,33]. Known amounts of adsorbent were added to 250 ml of Al (III) solution (known concentrations) taken in stoppered 500 ml conical flask. The initial pHs of the resulting solutions were adjusted to desired values using pH meter and by the addition of either dil. HCl or dil. NaOH. Then the conical flasks were agitated for a definite time in mechanical agitators. After a certain equilibration time, the adsorbent was separated from the water using filtration. The remaining (un-adsorbed) amount of Aluminum ions in the filtrate was assayed using the “Eriochrome cyanine R” method. [34]

By gradually changing the various physicochemical parameters namely, pH of the equilibrium mixture, equilibration time, adsorbent concentration, initial adsorbate concentration and working temperature, the optimum conditions for the maximum removal of Al(III) was assessed. The observed results with respect to these parameters were presented in Fig.-2 to 6. The effect of co-ions on the extraction of Al^{3+} was studied by keeping the concentration of co-ions in ten-fold excess than the concentration of Al^{3+}. The common ions that naturally existing were chosen for the study. The results are present in Fig.-7. The adsorption nature and adsorption kinetics were analyzed adopting well-known models and also thermodynamic studies were made. The observed results are depicted in Fig.-6 and Tables- 1 to 3. The developed method was applied to water samples collected at Aluminum Industry effluents and polluted lake waters and the observations are presented in Table-4.

RESULTS AND DISCUSSION

Using COSP as an adsorbent, the extraction of Al^{3+} ions was studied by gradually varying the extraction parameters. The following observations are significant

Effect of Agitation Time

The influence of time of equilibration on the extraction of aluminum ions at various solution pHs while keeping constant the sorbent dosage (2.5 g/L) and initial Al (III) concentration of Al ions (50 ppm), is studied and the results are presented in Fig.-2. At a fixed pH, as the equilibration increases, % removal of Al (III) is increased. For instance, at pH: 8, % removal is: 61% at 10 mins, 72 % at 20 mins, 92% at 30 mins, 96% at 60 mins, 98% at 90 mins, 100% at 120 mins and above.

The effect of Initial pH

The influence of the initial pH of the equilibration mixture on Al^{3+} ions extraction is presented in the Fig.-3. Maximum extractions are noted when the pH is between 6 to 8. Decrease or increase the pH from this optimum range, results in the decrease of % removal of Al^{3+} ions. The extractability (at constant *COSP* dosage: 2.5 g/L; agitation time: 120 min) is 56% in 1.0N HCl and is increased to 64.0% in 0.5N HCl. Percentage extraction is noted to be 78 at pH: 1, 90 at pH: 2, 95 at pH: 4 and reached 100% between pH: 6 to 8. With further increase of pH, the extractability is decreased: 85.0% at pH: 9 and 75.0 at pH. 10.

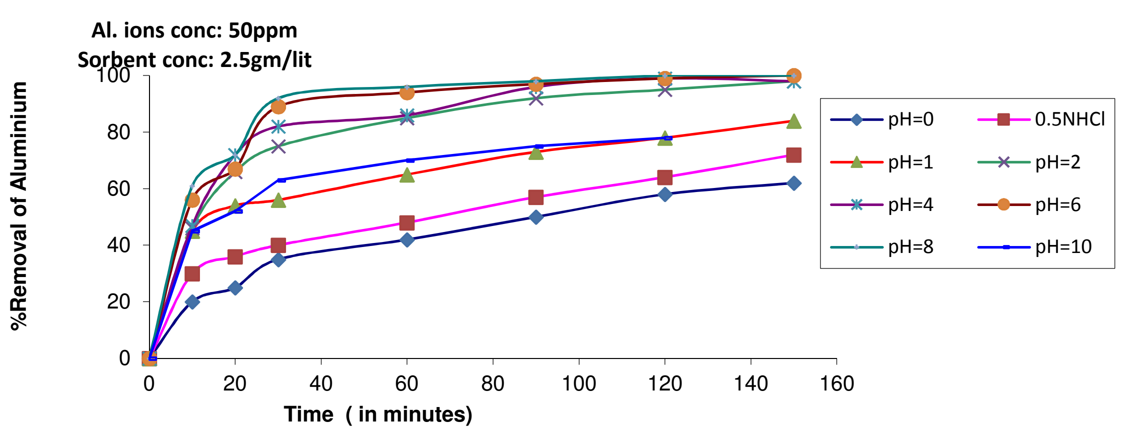

Fig.-2: Time Vs % Removal of Al^{3+} Ions

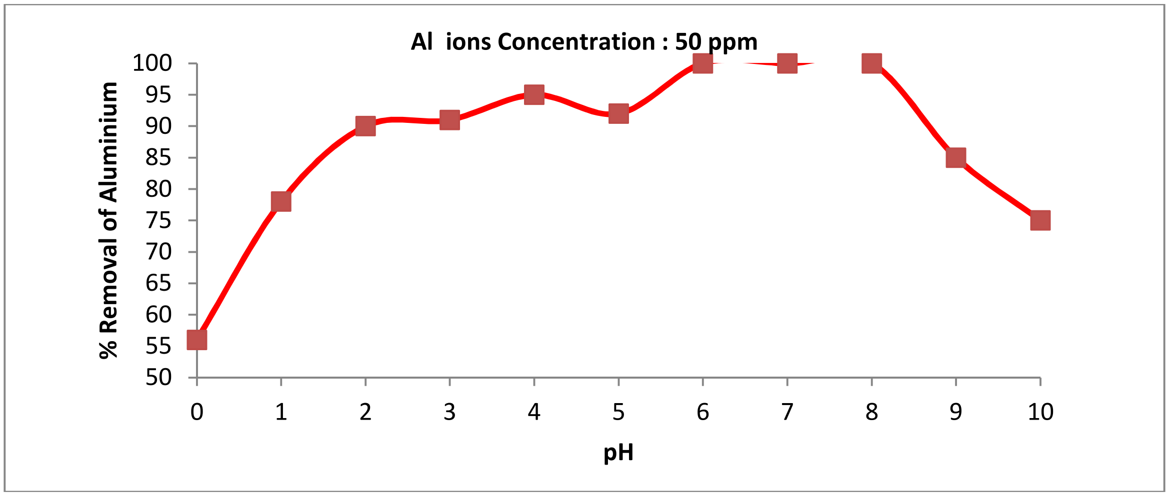

Fig.-3: pH Vs % Removal of Aluminium using COSP

Sorbent Concentration

The influence of adsorbent dosage on the extractability of Al(III) ions is studied. The observations are presented in Fig.-4. As the COSP concentration is increased, the % of extraction is also increased: 60.0% at 0.5 g/L; 70% at 1.0 g/L; 75.0% at 1.5 g/L; 95% at 2.0 g/L and 100% at and above 2.5 g/L. Initially, the % removal is more and it is slow down with the increase in the concentration of COSP and a study state is reached at and above 2.5 g/L with 100% removal of Al (III) ions.

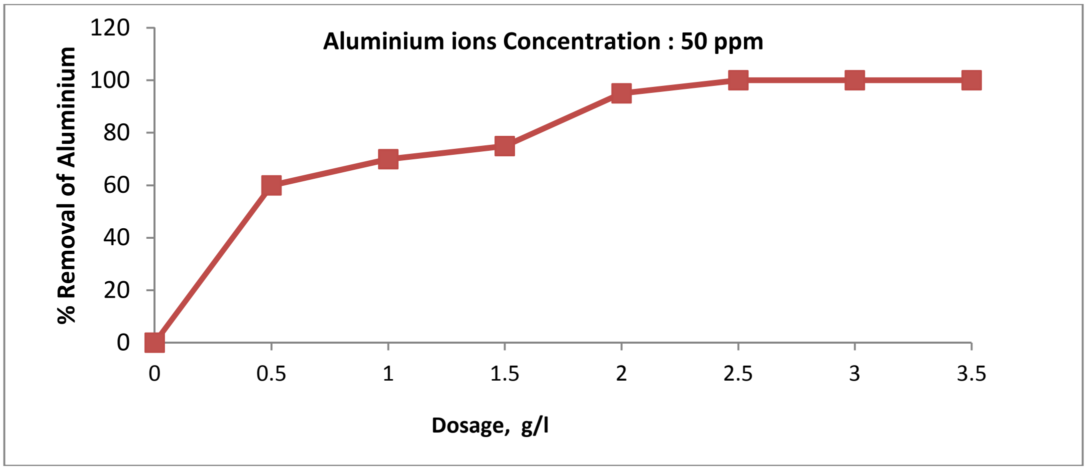

Fig.-4: Dosage Vs % Removal of Aluminium (III) using COSP

Initial Concentration Effect

The influence of initial concentration of Al(III) on the extraction of Al(III) ions is studied by changing the concentration of Aluminum ions from 20 mg/L to 100 mg/L while maintaining the other extraction conditions at optimum levels namely, pH: 8, equilibration time : 120 min, COSP dosage: 2.5 g/L, rpm: 300 and temp.: 30°C ± 2°C. The results obtained are depicted in Fig.-5. The % removal is 100% until the initial Al^{3+}concentration is 50 mg/L but when it is increased more than 50 mg/L, the % removal is decreased to: 90.0% at 60 mg/L; 82.0% at 70 mg/L; 75.0% at 80 mg/L; 68.0% at 90 mg/L; and 65.0% at 100 mg/L. At low concentrations of Al^{3+}ions, the availability of active sites for adsorption on COSP is more and hence the removal is more. As the concentration of Al^{3+} ions is progressively increased, the demand for active sites is increased. But for a fixed amount of COSP, the needed active sites are not sufficiently available and so, the less removal.

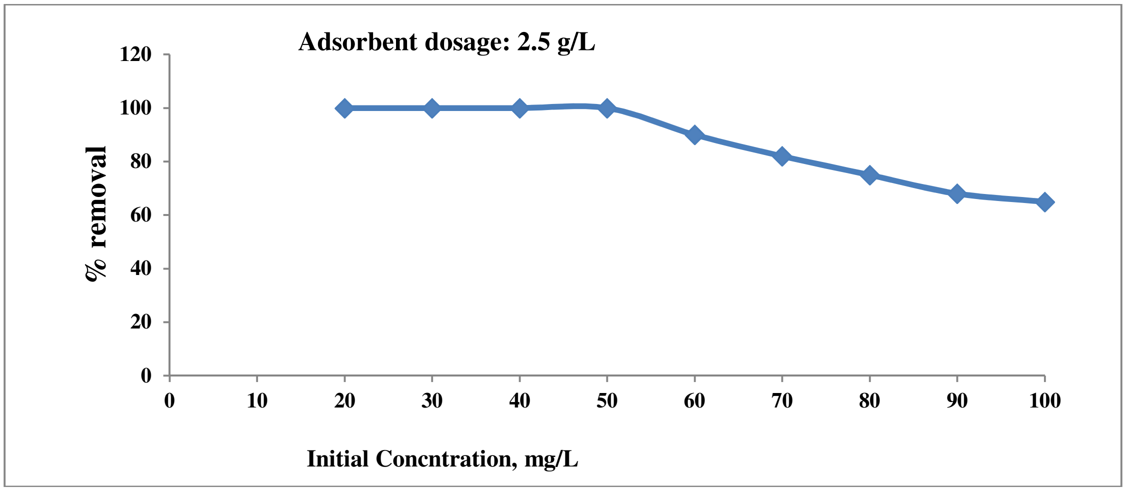

Fig.-5: Initial Concentration of Al(III) Ions Vs % Removal of Al(III

Influence of Temperature

Percentage extraction of Al^{3+} ions was studied at three temperatures: 303, 313 and 323 K.. The results are depicted in Fig.-6. It is observed that with a rise in temp from 303 to 323K, the percentage removal of Al ions increases from 92.6% to 97.2%. The results are presented in Fig.-6 and the calculated thermodynamic parameters in Table-1. Thermodynamics parameters namely ΔG , ΔH and ΔS were determined as per the equations: $\Delta G = -RT \ln K_d$; $\ln K_d = \Delta S/R - \Delta H/RT$; $K_d = q_e/C_e$ and $\Delta G = \Delta H - T\Delta S$ where K_d = the distribution coefficient for the adsorption, q_e = the amount of Al^{3+}ions adsorbed per liter of solution at equilibrium, C_e = the equilibrium conc. of Al^{3+}ion solutions, T = absolute temp. R = gas constant [17,20,28]. 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 ΔG = ΔH-TΔS and presented in Table-1. [28,33]

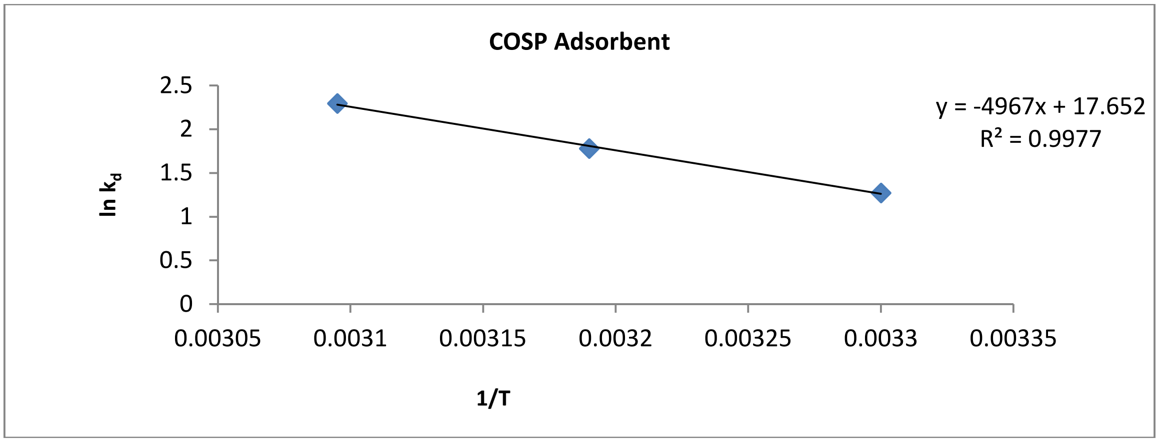

Fig.-6: 1/T Vs ln K_d

Table 1: Thermodynamic Parameters

Parameter	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)			R^2
Temperature(K)			303	313	323	
Bark Powder	41.295	146.75	-3.169	-4.6377	-6.105	0.9977

The positive ΔH and R^2 value close to one, indicate that the adsorption process is physisorption in nature and also that the process is endothermic[35]. The disorder and randomness at the surface of the adsorbent are indicated by the positive ΔS value. The spontaneity of adsorption is indicated by the negative value of ΔG. The adsorption forces are conducive to make the Al ions to cross the potential barrier at the interface of the adsorbent surface and solution. With the increase in temperature, the surface thickness of the adsorbent decreases while movement of Al ions towards the surface of the adsorbent increases and these two aspects increase the diffusion of Al ions into the surface layers of the adsorbent and also into the pores in the sorbents. This penetration results in the adsorption of more Al ions.

Analysis of Nature of Adsorption

The adsorption nature is studied adopting Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms[17, 20, 28 34] and the observations are noted in Table-2. It is inferred from the Table that the Langmuir model describes well the adsorption process than any other model as its R^2 = 0.9689 is near to unity than the rest. Hence, adsorption is monolayer and homogenous in nature. Moreover, the R_L value: 0.0212 indicates that the adsorption process is favorable as suggested by Hall et al [36]. Further, the values of E: 5.0KJ/mol and B: 2.3586J/mol of Temkin and Dubinin- Radushkevich equations, suggest that the adsorption is 'physisorption' (nonspecific Vander Waals forces) as the E value is < 8 kJ/mol and B values is >20 kJ/mole.

Table-2: Different Parameters of Various Models for the Adsorption of Al^{3+} onto COSP

S. No.	Adsorption Isotherms		Slope	Intercept	R^2
1	Langmuir isotherms	R_L 0.0212	0.0456	-0.0315	0.9689

2	Freundlich isotherms		0.2123	1.0558	0.8591
3	Temkin Isotherm	B: 2.3586J/mol	2.3586	14.304	0.8684
4	Dubinin-Radushkevich isotherm	E : 5.0KJ/mol	-4E-08	-7.1054	0.8942

Adsorption Kinetics

Pseudo-first-order, pseudo-second-order, Bangham's pore diffusion model, Elovich model and Weber and Morris intra-particle diffusion model are applied as described in the literature[17, 20,37-40] From the plots, various parameters were calculated. The values are noted in Table-3.

Table-3: Various Kinetic Parameters Pertaining to the Adsorption of Al^{3+} onto COSP

S. No.	Model	Slope	Intercept	R^2
1	Pseudo first-order	-0.0091	0.7833	0.9882
2	Pseudo second-order	0.0489	0.1804	0.9996
3	Bangham's pore diffusion	0.7454	-1.275	0.940
4	Elovich model	3.249	3.304	0.981
5	Weber-Mories Intra Particle Diffusion model	0.3038	16.2	0.765

It is revealed from the Table that the Pseudo-second-order model is a better fit model as its R^2.value: 0.9996 is more than the other models. Of these models, the Weber and Morris diffusion model is the least fit.

Interfering Ions

The interference caused by co-ions (in ten fold excess) that naturally exists in water, namely, SO_4^{2-}, NO_3^-, Cl^-, PO_4^{3-}, F^-, bicarbonate, Ca(II), Cu(II), Mg(II), Zn(II) and Ni (II) ions, has been investigated. The observations are noted in Fig.-7a and b . Sulphate, Nitrate and carbonate have marginally effected while Chlorides and Fluorides markedly interfered. But, phosphates synergistically maintained the extraction at 100%. *The* cations interfered in the order*:* $Zn^{2+} > Ni^{2+} > Cu^{2+} > Ca^{2+} > Mg^{2+}$.

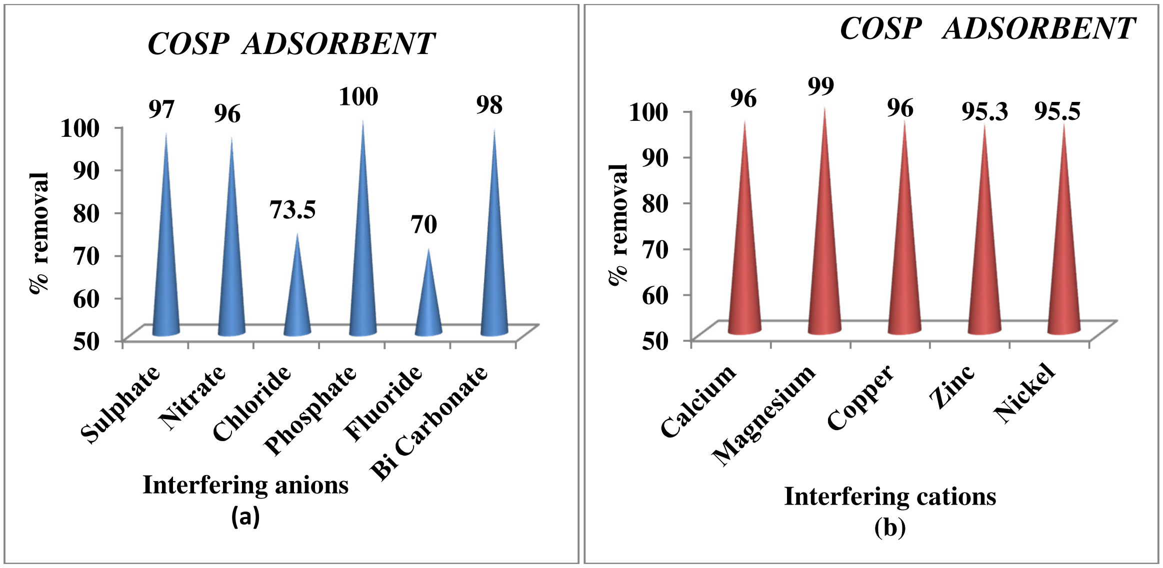

FIg.-7: (a) Effect of Interfering Anions on Adsorption of Al (III) FI. (b) Effect of Interfering Cations on Adsorption of Al (III)

Regeneration and Reuse

If the spent adsorbent is regenerated and reused, the cost of the procedure is effectively decreased. So, the regeneration of spent COSP is investigated using various eluting agents. It is found that 0.1 M NaOH is successful. As is evident from the Fig.-8, loss of efficiency of spent COSP is marginal until 4 recycles of regenerations. And hence, COSP can be reused up to four cycles. The % removal Al (III) ions is found to be 100.0 %, 98.0%, 97.0%, 96.0%, 84%, 76%, 65% and 50.5% respectively for 1 to 8th regenerations.

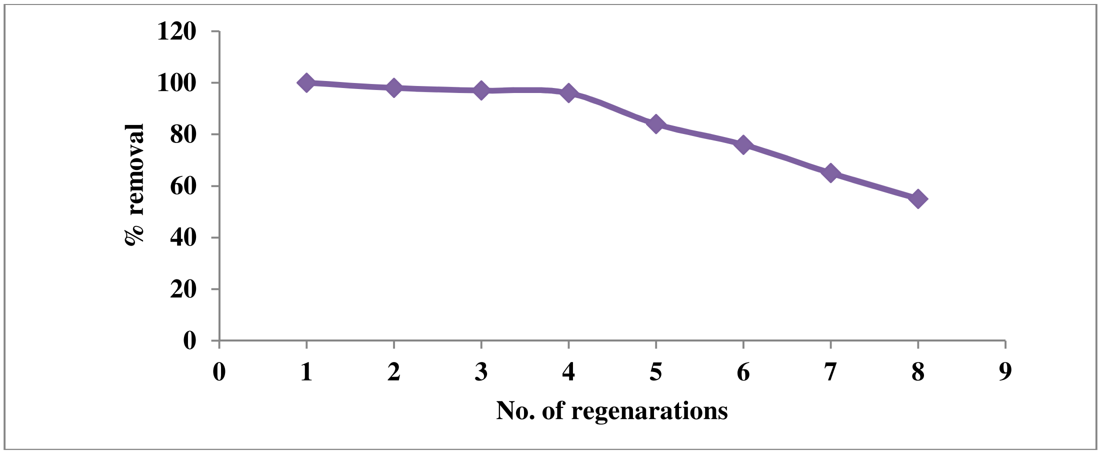

Fig.-8: No. of Regeneration Vs % Removal

Applications

The validity of procedure developed in the present work was investigated by applying it to real polluted water samples collected at diverse sources namely, Aluminum based industries and also from the naturally contaminated water. Results are presented in Table-4.

Table- 4: Removal of Al(III) from Polluted Water Samples
(pH:8; COSP dosage: 2.5 g/L, time of equilibration: 120 min, rpm:300 and temperature 28°C±2°C)

Samples	Initial Al $^{3+}$ conc. (in mg/L)	Al $^{3+}$ conc. after extraction (in mg/L)	Percentage removal
Alum Industry effluents			
1	10.5	0.5	95.2%
2	12.3	0.6	95.1%
3	14.1	0.8	94.3%
Polluted Lake Samples (having known conc. of Al^{3+}):			
1	15.0	0.9	94.0%
2	20.0	1.4	93.0%
3	25.0	1.8	92.8%

As is evident from the data that good amounts of Al (III) are extracted and hence, the adsorbent can be used in the treatment of wastewater/ industrial effluents.

CONCLUSION

An adsorbent derived from *Cassia Occidentalis* plant stems is investigated for the extraction of Al^{3+} ions from wastewater by optimizing the extractions conditions namely, pH, adsorbent dosage, contact time, initial conc. of Al^{3+} ions and temperature. With simulated water, 100% removal of Al ions is observed in the pH range 6-8 and with sorbent conc: 2.5 g/L, equilibration time: 120 min and temp 30^0 C. Common co-cations and many anions (except Cl$^-$ and F$^-$) have only marginal interference. It is interesting to note that substantial amounts of Al ions are extracted even at low pH values. This paves the way to apply this method even for acidic polluted water. The adsorption kinetics and nature of adsorption are investigated. Thermodynamic parameters are evaluated. The method developed is effectively applied for removing Al(III) ions from the industrial effluents and polluted samples. The adsorbent can be regenerated and reused up to four cycles.

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