Removal of aluminium (III) from waste waters using bio-sorbents pertaining to Withania somnifera plant

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ABSTRACT

Removal of Aluminum (III) from waste waters using bio-adsorbents derived from plant materials of Withania somnifera has been investigated by varying various physicochemical parameters such as pH, time of equilibration, sorbent dosage, agitation time, initial concentration of Aluminum ions, temperature and presence of foreign ions using simulated waters and by adopting batch methods of extraction. Optimum conditions for the maximum extraction of Al (III) ions have been investigated. The adsorption process is analyzed with Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherm models and found that the Langmuir isotherm model better describes the adsorption process emphasizing the mono-layer formation of the Al (III) ions on the adsorbent and further, the mean free energy (E) and heats of sorption (B) of Temkin isotherm and Dubinin-Radushkevich isotherms indicate that the adsorption is 'physisorption' in nature. Kinetics of adsorption is quantified using pseudo first-order, pseudo second-order, Weber and Morris intraparticle diffusion, Bangham's pore diffusion and Elovich equations and found that the adsorption process has good correlation coefficient values with pseudo-second-order model. The endothermic nature of the adsorption is found on the analysis of the thermodynamic parameters, ΔH, ΔS and ΔG. Interference of common co-ions has been studied. The methodologies developed are successfully applied to industrial sewages and polluted natural waters.

Key words: Aluminum (III), pollution control, bio-sorbents, kinetics, adsorption isotherms, Withania somnifera

INTRODUCTION

Exploring the adsorption abilities of bio-sorbents derived from plant materials towards different pollutants in the removal of the latter from waste or polluted waters is being increasing investigated throughout the Globe. Our research group has been investigating on these bio-methods of pollution and successfully developed methods for the removal of Chromium (VI) (1-4), Zinc (5,6), Aluminium (III) (7-10), Fluoride (11-17), Nitrite (18,19), Nitrates (20), Ammonia(21-23),Phosphate (24,25) and Dyes (26 -29). Further, bio-remediation methods are developed for the control of metal ions using oxidation ponds and different bio-masses (30). In the present work, bio-sorbents derived from plant material of Withania somnifera plant have been investigated for their effectiveness in the removal of toxic Aluminium (III) ions from polluted waters.

The presence of Aluminum (III) in water-bodies is harmful to aquatic life and it a neurotoxin (31) and its consumption by human beings, results in serious disorders such as kidney disorders, Parkinson and Alzheimer’s disease (32), mellowing of bones (33), effecting the eye sight, pulmonary fibrosis and microcytic anemia (34). Hence, as per WHO and US drinking waters standards, the maximum permissible limit of Aluminium (III) is: 0.2 ppm. Inadequately treated effluents from industries pertaining to food and beverages, dyeing, textile and drugs and residual aluminium in treated municipal waters, are the main source of contamination. Further, nearly 7% of Aluminium present in the earth’s crust is leached into the nearby water bodies under acidic conditions and it becomes detrimental to the biota, micro-organisms and human beings.
The methods based on aeration/stripping, sedimentation and filtration are ineffective at micro levels and methods based on ion-exchange, reverse osmosis Electrodialysis are expensive (35-38). The non-conventional methods based on bio-adsorbents are being used in removing Aluminium ions from polluted waters. Algal biomass (39), powdered marble wastes (40), combination of active carbon as adsorbent and oleic acid as surfactant (41) water hyacinth (42), Chitosan (43), rice husk char and activated rice husk char (35,44) have been investigated for the removal of Aluminium ions from waste waters. Bio-absorbents derived from Acacia Melanoxylon and Eichhornia Crassipes Plants (7), Moryngea Millingtonia and Cygium Arjunum Plant (9), Achiranthus aspera and Cassia Occidentalis (10), have been successfully used to remove Aluminium (III) from polluted waters.

In the present work, bio-adsorbent derived from leaves and stems of Withania somnifera plant have been investigated by varying various physicochemical parameters to optimize the conditions of extraction for the maximum removal of Aluminium ions from polluted waters.

MATERIALS AND METHODS

Bi-adsorbent derived from the leaves and stems of Withania somnifera plant (Figure 1) are found to have affinity for Aluminum (III) ions. Withania somnifera (ashwagandha) is an herb in the Solanaceae family and it grows in wet lands. It has many medicinal values and this plants parts are used in the preparation of some Ayurvedic medicines in the cure of tumors, tubercular glands, carbuncles, and ulcers.

Figure 1: Withania somnifera plant

Adsorbents are prepared from the leaves and stems of Withania somnifera plant and are used in the extraction of Aluminium ions from polluted waters using batch methods of extraction (47-49).

Preparation of the Bi-adsorbents: The leaves and stems of Withania somnifera plant 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: < than 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.

Extraction Method: Weighted quantities of adsorbents were taken in to previously washed 1 lit/500 ml stopper bottles containing 500ml/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 (50). In this work all chemical used were of analytical grade and double distilled water was used for the preparation of solution.

The sorption nature of the bio-adsorbents were studied by varying physicochemical parameters such as pH, time of equilibration, initial concentration of the adsobate, adsorbent dosage and temperature. The results were presented in the Graph No. 1 to 13 and Table 1-3.

Effect of Co-ions: The presence of tenfold excess of common co-ions on the % of extraction of the Aluminium ion was studied at other optimum conditions of extraction as inferred from the Graph No. 1-3 and the results were presented in the Table: 4.
RESULTS AND DISCUSSION

It is observed that the % of extraction is affected by pH, time of equilibration, sorbent dosage, temp., and initial concentration of the adsorbate.

A: Effect of Time of Equilibration:
With the increase in time of equilibration, % removal of Aluminium ions also increases and after certain time, no more adsorption is found (vide Graph Nos. A: 1-a to 1-d). For instance, at other optimum conditions of extraction, % removal is found to be: 58% at 10 minutes, 68 % at 20 minutes, 76% at 30 minutes, 82% at 60 minutes, 90% at 90 minutes, 98% at 120 minutes and 100% at 150 minutes or above with the bio-adsorbents pertaining to leaves powders (vide Graph No.1-a). The optimum time for agitation is found to be 150 minutes for bio-adsorbent pertaining to the leaves and stems at optimum pH: 8 while it is 120 minutes with their ashes. (vide Graph No: 1)
B: Effect of pH: The optimum pH is found to be between 6 to 8 (Vide Graph: 2). 100% of removal of Aluminium is observed with all the bio-adsorbents developed in this work when all other conditions of extractions are optimized namely: equilibration time : 150 minutes and sorption dosage: 2.5gm/lit for leaves powders; equilibration time of 120 minutes and sorption dosage: 2.0 gm/lit for leaves ashes; equilibration time : 150minutes and sorbent dosage:2.0gm/lit for stems powder and equilibration time of 120 minutes and sorbent dosage :1.5gm/lit for stem ashes.

C: Sorbent Dosage: The optimum sorbent dosage is found to be 2.5 gram/lit for the leaves bio-adsorbent and 2.0 gm/lit with its ashes. With stems bio-adsorbent, the dosage is found to be: 2.0gm/lit and 1.5 gm/lit. with their ashes (vide Graph No : 3:)

Graph Nos. 1-c & d: Removal of Aluminum (III) Vs Time of Equilibration with stem based bio-adsorbents of Withania Somnifera plant.
D: Effect of Temperature:
The influence of temperature on the extraction of Aluminum was investigated at 303, 313 and 323K with simulated 5.0 mg/l Aluminum solutions and at other optimum conditions of extractions. The observations are presented as ln Kd Vs 1/T as shown in Graph No.4-a to 4-d. Thermodynamic parameters free energy (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 [51-53], ΔG = -RT ln Kd, ln Kd = ΔS/R - ΔH/RT; Kd = qe/Ce and ΔG = ΔH – TΔS, where Kd is the distribution coefficient for the adsorption, qe is the amount of Aluminum ion adsorbed on the adsorbent per liter of solution at equilibrium, Ce is the equilibrium concentration of Aluminum(III) ion solution, T is the absolute temperature in Kelvin, R is the gas constant. The values of ΔH and ΔS were obtained from the slope and intercept of a plot between ln Kd and 1/T and ΔG values were obtained from the equation ΔG = ΔH-TΔS and tabulated (vide Table 1) [54, 55].

As the temperature increases from 303 to 323K (30 to 50°C), the % extraction Aluminum(III) ion increases from 71.5 to 75.5% in the case leaves bio-sorbent; 80.0 to 86.5% with ashes of leaves; 74.5 to 79.5% with stems bio-sorbent; 83.0 to 88.5% with stems ash. With the increase in temperature, the diffusion of Al3+ into the surface layers of the adsorbent is more facilitated due to the increase in K.E. of the ions and decrease in the density of outer surface of the adsorbent.

From the Table 1, it can be inferred that the adsorption process is:
- endothermic in nature as the R² is near to “one” and ΔH is positive
- physisorption as the ΔH is positive [56]
- increased disorder and randomness at the solid solution interface as the ΔS is positive [57].
- spontaneous nature as ΔG is negative [58].

E: Adsorption Isotherms:
Freundlich [59], Langmuir [60], Temkin [61] and Dubinin-Radushkevich [62] isotherms are used to evaluate the nature of adsorption.

Linear form of Freundlich equation is \( \log (q_e) = \log k_f + \frac{1}{n} \log C_e \) and Langmuir equation is \( C_e/q_e = \frac{(a_L/k_L)C_e}{1 + a_LC_e} \). Significant feature of the Langmuir isotherm model is the dimensionless separation factor, \( R_L = \frac{1}{1 + a_LC_e} \). According to Hall et al [63], the nature of the adsorption process is unfavorable if \( R_L > 1 \), linear if \( R_L = 1 \), favourable if \( 0 < R_L < 1 \) and irreversible if \( R_L = 0 \).

The linear results are presented in Graph. No 5-a to d & 6-a to d and isothermal constants along with the correlation coefficient values are presented in Table 2-A.
The high correlation coefficient ($R^2=0.9985$, 0.9938, 0.9689 and 0.9983) values than Freundlich isotherm and dimensionless separation factor ($R_\text{L}= 0.0159, 0.0142, 0.0212$ and 0.01174) values in the range of 0-1, suggest that the favorable model for the adsorption process is Langmuir isotherm, and hence indicates the monolayer coverage of the adsorbent surface with the adsorbate is favorable.

Graph Nos. 1-a & b: Removal of Aluminum (III) Vs Time of Equilibration with Leaves based bio-adsorbents of Withania Somnifera plant

Graph Nos. 1-c & d: Removal of Aluminum (III) Vs Time of Equilibration with stem based bio-adsorbents of Withania Somnifera plant

Table 2-A: Adsorption isothermal parameters of Freundlich and Langmuir plots on different bio-adsorbents of Withania somnifera plant

<table>
<thead>
<tr>
<th>S.No</th>
<th>Adsorption isotherms</th>
<th>Bio-sorbent</th>
<th>Slope</th>
<th>Intercept</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Freundlich isotherms</td>
<td>Leaf Powder</td>
<td>0.223</td>
<td>0.9485</td>
<td>0.8868</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf ash</td>
<td>0.2033</td>
<td>1.0761</td>
<td>0.8605</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem Powder</td>
<td>0.2123</td>
<td>1.0558</td>
<td>0.8591</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem ash</td>
<td>0.1453</td>
<td>1.2408</td>
<td>0.9087</td>
</tr>
<tr>
<td>2</td>
<td>Langmuir isotherms</td>
<td>Leaf Powder</td>
<td>0.01594</td>
<td>0.0545</td>
<td>0.0341</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf ash</td>
<td>0.0142</td>
<td>0.0463</td>
<td>0.0259</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem Powder</td>
<td>0.0212</td>
<td>0.0456</td>
<td>-0.0315</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem ash</td>
<td>0.001174</td>
<td>0.0352</td>
<td>0.0219</td>
</tr>
</tbody>
</table>

Further, the adsorption process is modeled with Linear form of Temkin equation: $q_e = B \ln C_e + BlnA$ where $RT/b = B$; Linear form of Dubinin-Radushkevich equation : $\ln q_e = -\beta\varepsilon^2 + \ln q_m$, where $\varepsilon = RT \ln(1+1/C_e)$. The linear plots of these two adsorption isotherms are depicted in Graph.No :7-a to d & 8-a to d and isothermal constants along with the correlation coefficient values are presented in Table 2-B.
Graph No: 2: pH Vs. %of Removal of Al (III)

Graph No: 3: Dosage Vs % of removal of Al (III)

Graph No: 4-a

Graph No: 4-b
Graph Nos 4-a to 4-d: Effect of temperature on % removal of Aluminium(III) ion with different Sorbents

Graph No. 5-a to 5-d: Freundlich isotherms of Different Bio-adsorbents
Graph Nos. 6-a to 6-d Langmuir isotherms with different Bio-sorbents

Table 2-B: Adsorption isothermal parameters of Temkin and Dubinin Radushkevich plots on Bio-sorbents of Withania somnifera

<table>
<thead>
<tr>
<th></th>
<th>Temkin Isotherm</th>
<th>Dubinin-Radushkevich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>Slope</td>
</tr>
<tr>
<td>Leaf Powder</td>
<td>2.271J/mol</td>
<td>2.271</td>
</tr>
<tr>
<td>Leaf ash</td>
<td>2.227J/mol</td>
<td>2.227</td>
</tr>
<tr>
<td>Stem Powder</td>
<td>3.5833J/mol</td>
<td>3.5833</td>
</tr>
<tr>
<td>Stem ash</td>
<td>4.012J/mol</td>
<td>4.012</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>Slope</td>
</tr>
<tr>
<td>Leaf Powder</td>
<td>5.0KJ/mol</td>
<td>-2E-08</td>
</tr>
<tr>
<td>Leaf ash</td>
<td>1.2909KJ/mol</td>
<td>-3E-07</td>
</tr>
<tr>
<td>Stem Powder</td>
<td>5.0KJ/mol</td>
<td>-2E-08</td>
</tr>
<tr>
<td>Stem Ash</td>
<td>3.162KJ/mol</td>
<td>-5E-08</td>
</tr>
</tbody>
</table>
$R^2$-values near to unity indicate the applicability of these two model adsorption isotherms confirming the heterogeneous surface of the adsorbent. The mean free energy ($E$) and heats of sorption ($B$) are characteristics of adsorption and as $E$ values are less than 8 kJ/mol and $B$ are less than 20 kJ/mol, the adsorption is “physisorption” in nature i.e. non-specific adsorption due long range weak Vander Waals forces [64-68].

**F: Adsorption Kinetics**

Kinetics of adsorption is studied using pseudo first-order model [69, 70], pseudo second-order model [70, 71], Weber and Morris intraparticle diffusion model [72], Bangham’s pore diffusion model[73] and Elovich equations[74,75]. The pseudo first-order equation is $\log (q_e - q_t) = \log q_e - k_1 t/2.303$; the pseudo second-order equation is $t/q_t = 1/k_2 q_t^2 - (1/q_e) t$; Weber and Morris intraparticle diffusion equation is $q_t = k_p t^{1/2} + c$; Bangham’s pore diffusion equation is $\log [\log (C_i/C_i-q_t)] = \log (k/2.303) + \alpha \log(t)$; Elovich equation is $q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t)$

The data of these five kinetic models are presented in Graph Nos: 9-a to d, 10-a to d, 11-a to d, 12-a to d & 13-a to d and rate constants along with the correlation coefficient values are presented in Table 3.
Graph. No: 9-a to 9-d Pseudo second-order model for different bio-sorbents

- **Leaf Powder of Withania Somnifera**
  \[ y = -0.0097x + 1.0087 \]
  \[ R^2 = 0.9464 \]

- **Leaf Ash of Withania Somnifera**
  \[ y = 0.0138x + 0.0336 \]
  \[ R^2 = 0.9775 \]

- **Leaf Powder of Withania Somnifera**
  \[ y = -0.0138x + 1.0336 \]
  \[ R^2 = 0.9978 \]

- **Leaf Ash of Withania Somnifera**
  \[ y = -0.0109x + 1.0425 \]
  \[ R^2 = 0.9978 \]

Graph. No: 10-a & b: Pseudo second-order model for Leaf Bio-sorbents

- **Leaf Powder of Withania Somnifera**
  \[ y = 0.0464x + 0.639 \]
  \[ R^2 = 0.9972 \]

- **Leaf Ash of Withania Somnifera**
  \[ y = 0.0384x + 0.2533 \]
  \[ R^2 = 0.9993 \]
Graph No: 10-c: Pseudo second-order model for Stem Bio-sorbents

Graph No: 10-d

Graph No 11-a to 11-d: Weber and Morris intra particle diffusion for different adsorbents of Withania Somnifera
Graph No:12-a to 12-d Bangham’s pore diffusion for different bio-sorbents of Withania somnifera

Leaf Powder of Withania Somnifera

\[ y = 0.5114x - 0.8228 \]

\[ R^2 = 0.9027 \]

Leaf Ash of Withania Somnifera

\[ y = 0.7183x - 1.1277 \]

\[ R^2 = 0.9611 \]

Graph No:12-a

Graph No:12-b

Leaf Powder of Withania Somnifera

\[ y = 0.5665x - 1.0486 \]

\[ R^2 = 0.9344 \]

Leaf Ash of Withania Somnifera

\[ y = 0.6912x - 1.1522 \]

\[ R^2 = 0.9685 \]

Graph No:12-c

Graph No:12-d

Graph No:13-a & b: Elovich model Leaf based bio-sorbents of Withania Somnifera plant

Leaf Powder of Withania Somnifera

\[ y = 3.9124x + 5.0194 \]

\[ R^2 = 0.9709 \]

Leaf Ash of Withania Somnifera

\[ y = 3.6007x + 0.8782 \]

\[ R^2 = 0.9781 \]

Graph No:13-a

Graph No:13-b
On perusal of the correlation coefficient ($R^2$) values, it may be inferred that the kinetics of adsorption follows the order: pseudo second-order > Elovich model > pseudo first-order > Bangham’s pore diffusion > Weber and Morris intraparticle diffusion. Hence, the adsorption kinetics can be well defined by pseudo second-order and least by Weber and Morris intra-particle diffusion model.
The effect of the presence of tenfold excess of common co-ions viz., Sulphate, Nitrate, Chloride, Phosphate, Fluoride, Carbonate, Calcium, Magnesium, Copper, Zinc and Nickel ions on the % removal of Aluminium ions from synthetically simulated waters has been studied and the results are presented in Table No.4.

Cations have marginal effect and % of removal never comes down below 91.0% (Vide Table 4: Columns: 10-14).

Anions like SO$_4^{2-}$, NO$_3^-$ and CO$_3^{2-}$ marginally affected the % of extraction but Chloride and Fluoride affected the % of extraction significantly but Phosphates synergistically maintained at 100% of extraction.

APPLICATIONS

The methodologies developed in the present investigation have been applied to the samples collected from industrial effluents and polluted natural waters and the results are presented in the Table No: 5. It is inferred from the Table that the methods developed are successful as more than 90.0% of extraction is observed.

<table>
<thead>
<tr>
<th>SAMPLES COLLECTED AT DIFFERENT PLACES</th>
<th>Conc. of Al(III) in the Sample</th>
<th>% of Maximum extraction of Aluminium(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--------------------------------------</td>
<td>-------------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>Alum  Industry effluents:</td>
<td></td>
<td>Withania somnifera</td>
</tr>
<tr>
<td>1</td>
<td>20.0 ppm</td>
<td>Leaves Powders (mesh:75 µ)</td>
</tr>
<tr>
<td>2</td>
<td>23.0 ppm</td>
<td>Leaves Ashes pH: 6;120 min &amp; 2.0 g/lit</td>
</tr>
<tr>
<td>3</td>
<td>30.5 ppm</td>
<td>Stem Powders (mesh:75 µ)</td>
</tr>
<tr>
<td>4</td>
<td>10.0 ppm</td>
<td>Stem Ashes pH: 6;120 min &amp; 1.5 g/lit</td>
</tr>
<tr>
<td>5</td>
<td>15.0 ppm</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>22.5 ppm</td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSION

- Bio-adsorbents from the leaves and stems of Withania somnifera plant have been prepared. Their affinity towards the removal of Aluminum (III) has been investigated with respect to pH, time of equilibration, sorbent dosage, agitation time, initial concentration of Aluminum ions, temperature, and presence of co-ions using simulated waters and by adopting batch methods of extraction. Optimum conditions for the maximum removal have been established. The interference of the common co-ions present in waters on the % of extraction, has been studied

- The adsorption process is analyzed with Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherm models and found the suitability of the Langmuir isotherm model indicating the mono-layer formation of the adsorbate on the adsorbent. The 'Physisorption' nature of the adsorption process has been inferred from Temkin and Dubinin-Radushkevich isotherm models and by calculating the mean free energy (E) and heats of sorption (B) form the plots of the isotherms.
The kinetics of adsorption process has been analyzed using pseudo first-order, pseudo second-order, Weber and Morris intraparticle diffusion, Bangham’s pore diffusion and Elovich equations and found that the adsorption process is well described by the pseudo-second-order model.

The endothermic nature of the adsorption is found on the analysis of the thermodynamic parameters, ΔH, ΔS and ΔG.

The methodologies developed are successfully applied to industrial sewages and polluted natural water samples.

Acknowledgement
The authors thank UGC for financial aid for conducting this research work.

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