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Removal of Chromium (VI) from Waste Waters Using Leaves Powders of Justicia adhatoda, *Cissus quadrangularis*, Soapnut Acacia

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ABSTRACT

The sorption characteristics of bio-adsorbents derived from leaves of Justicia adhatoda , Cissus quadrangularis, Soapnut Acacia toward Chromium (VI) ions , have been explored by varying the physicochemical parameters such as pH, sorbent concentration and time of equilibration. Percentage of extraction of Chromium (VI) is found to be pH sensitive and also depends on time of equilibration and sorbent concentration. Conditions have been optimized for the maximum extraction of Chromium (VI); it is found to be: 88.0% with Justicia adhatoda leaves powders; 88.0% with Cissus quadrangularis leaves powder, and 84.0% with Soapnut Acacia leaves powders. Tenfold excess of common cation ions are found to have synergistic effect in enhancing the % removal of Chromium(VI). SO_4^{2-}, PO_4^{3-} *and* CO_3^{2-} *are interfering in the order:* $PO_4^{3-} > SO_4^{2-} > CO_3^{2-}$. NO_3^-, Cl^- *and* F^- *have marginal interference. The methodologies developed in this work are remarkably successful in removing the Chromium(VI) from industrial effluents and polluted lake samples.*

Key Words: Removal of Chromium (VI), Bio-sorption, Herbal plants, Applications.

INDTRODUCTION

Toxic chromium salts are extensively used in various industries such as leather industry metallurgical industries and in the manufacture of, paints, inks, wood preservatives, photographic materials, textile , rubber, ceramics and in fungicides[1 -3]. The effluents of these industries having have to be treated for the complete removal of Chromium ions before they are discharged into environment. If rigorous scientific methods of disposal are not followed, there arises a potential danger of entrance of Chromium ion into the nearby water bodies. The Chromium ions being non-degradable in nature enter into the biological systems, get accumulated in the food chains in unspecific compounds inside the cells of living organisms causing significant threat to aquatic life [3-6].

Of the two states of Chromium, hexavalent ions are many folds dangerous then trivalent ions It is due to its easy penetration into biological membranes resulting in health hazards [6] such as skin disorders, respiratory track problems, lung carcinoma, acute tubular necrosis of kidney and even death in extreme cases [2,3,6].

The permissible potable limit of Chromium in drinking waters is 0.1 ppm and in irrigation waters is 100 ppm as per USEPA [2, 3, and 6].

Methodologies have been developed in controlling Chromium, based on Chemical reduction [5,7-9], Flocculation[7], Electrolysis and Electroplating [10,11], Nanofiltration[12], bioaccumulation [13], ion exchange[14], adsorption on silica composites [15,16], activated carbons[17-19], fly Ash [20], modified zeolites [21,22], bone charcoal [23] and microbes [24] .A number of patents are also found in literature [25]. These techniques suffer from one or other disadvantages like costly, incomplete metal removal, high reagent and energy requirements and generation of toxic sludges or other toxic waste products that require careful disposal. An efficient, simple, eco-friendly and economical methods are still eluding the environmental researchers.

In this contest bioadsorbents derived from Lignocelluloses materials such as leaves, barks, biomasses, and other agricultural wastes in controlling pollution problems [26-37] are proving to be potential alternative to the traditional and conventional methods. Many biomaterials have been probed for their sorption abililties towards Chromium ions. Methods have been developed using coconut fiber [28], eucalyptus bark [30] , maple sawdust [31], *Hevea brasilinesis* sawdust activated carbon [32] , waste tealeaves, rice husk [33] and Neem Sawdust [35] . Comparative studies have also been made using different adsorbent in effectively controlling the Chromium in waters [36, 37]. A review of literature using microbes in extracting Chromium is available in literature [24].

While we are making some pilot studies in exploring the sorption abilities of powders of leaves of herbal plants for the removal of Chromium (VI) from polluted waters, we noticed strong affinity between Chromium ions and leaves powders of Justicia adhatoda,Cissus quadrangulari and Soapnut Acacia. The present work is a thorough study of sorption characteristics of these biomaterials towards Chromium(VI) in developing a simple and versatile procedures for its removal .

MATERIALS AND METHODS

(A) Chemicals:

All chemicals used were of analytical grade**.** 50 ppm stock solution of Chromium (VI) was prepared using A.R. Potassium Dichromate in double distilled water. 6N Sulphuric acid and 0.25% of Diphenyl carbazide in 50% of acetone were employed.

(B)Adsorbents: The sorption nature of powders of leaves of *Justicia adhatoda*, *Cissus quadrangularis* and *Soapnut Acacia* for Chromium (VI) have been studied in this work .

Justicia adhatoda ***Cissus quadrangularis*** **Soapnut Acacia**

Fig : 1: Plants showing affinity towards Chromium (VI)

Justicia adhatoda is a herbal plant blossoms in cold season and is called Vaidyamata Singhee in Sanskrit. It belongs Acanthaceae family and grows wild in abundance all over India. It is reported to have many medicinal values especially related to heart ailments.*Cissus quadrangularis* is a perennial plant of the grape family and is commonly known as Veldt Grape or Devil's Backbone. It is native to India and grows to a height of 1.5 m.It belongs to Vitaceae family. It has many therapeutic values in curing fractured bones, asthma and cardiac problems. Its products also reported to be useful in curing leprosky,ulcers, tumours and skin diseases. Soapnut Acacia is herb blongs to Mirnosaceae family and is well grown in costal planes of south India. Its plant material are used used as astringentand cleanser and also in the preparation some traditional Tribal Formulations. It is endowed with medicinal values in curing skin diseases, renal calculi, vesicle calculi, hemorrhoids, leprosy, abscesses, eczema and biliousness.

The leaves of *Justicia adhatoda*, *Cissus quadrangularis* and *Soapnut Acacia* were cut, washed with tap water followed by distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: <75µ and then employed in this study.

(C) Adsorption experiment:

Batch system of extraction procedure was **adopted [7-9]:** Carefully weighted quantities of adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500ml/250ml of Potassium Dichromate 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 allowed to be in equilibrium for the desired time. After the equilibration period, an aliquot of the sample was taken for Chromium determination. Chromium (VI) was determined Spectrophotometrically by using **"**Diphenyl Carbazide" method [38].

Estimation of Chromium (VI): An aliquot amount of Chromate sample was taken in a 100ml volumetric flask. To it, 1ml of 6N Conc. H_2SO_4 solution and 1ml of Diphenyl Carbazide solution were added successively and the solution was then diluted to the volume and mixed well. Then O.D. of the developed color was measure against blank at 540 nm using U.V. and Visible Spectrometer.

Thus obtained O.D Value was referred to a standard graph (drawn between O.D and Concentration) prepared with known amounts of Chromium by adopting the method of Least Squares to find concentration of Chromium in unknown solutions.

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

(D) Effect of Interfering Ions:

The interference of foreign ions: Sulphate, Nitrate, Chloride, Phosphate, Fluorides, Chloride, Carbonate, Calcium, Magnesium, Copper , Zinc, Nickel and Iron ions have been studied. The synthetic mixtures of Chromium (VI) and one of the interfering ions were so made that the concentration of the interfering ions were maintained at **ten**-fold excess than the Chromium (VI) ion concentration. 500 ml of these solutions were taken in stopped bottles and then correctly weighed optimum quantities of the promising sorbents as decided by the Graph No. C:1 were added. Optimum pH was adjusted with dil. HCl or dil. NaOH using pH meter. The samples were shaken in shaking machines for the desired optimum periods and then the samples were filtered and analyzed for Chromium (VI). Percentage of extraction of Chromium was calculated from the data obtained. The results were presented in the Table No. 1.

(E)Applications:

The procedures developed in this work, were applied to some real samples collected from three tannery industries in Hyderabad, three Chrome plating industries in Chennai and three polluted lakes at different places in Bapatla mandalam of Guntur Dt of Andhra Pradesh. The samples from industrial effluents were analyzed for Chromium contents and the lake samples were fed with known amounts of Chromium (VI).

Then these samples were subjected to extraction for Chromium (VI) using the bio-sorbents developed in this work at optimum conditions of pH, equilibration time and sorbent concentration. The results obtained were presented in the Table 2.

RESULTS

From the sorption data presented in the Graph No: A: 1-3; B: 1; C: 1 and Table No.:1 &2, the following points may be inferred:

1. The powders of leaves *Justicia adhatoda* ,*Cissus quadrangularis* and Soapnut Acacia have been found to be sensitive to Chromium (VI) ions at low pH values.

2. Percent of extractability is time dependent and progressively increases with time for a fixed adsorbent at a fixed pH and after certain duration, it remains constant; i.e. an equilibrium state has been reached. In other words, there

will not be any further adsorption after certain time of equilibration time (vide Graph Nos. A: 1-3). As for example, in the case of leaves of *Justicia adhatoda*, at pH: 2 and at sorption conc. of 2.5gm/500 ml, the % of extraction is : 28.0% at 0.5 hr; 44.0% at 1.0 hr; 64.0% at 1.5 hr; 84.0% at 2.0 hr; 88.0% at 2.5 hr; 88.0% at 3.0 hr; 88.0 % at periods more than 3.0 hrs. (Vide Graph No.: A: 1). The trend is same in rest of the sorbents (vide Graph No.: A: 2&3).

3. **Effect of pH:** pH conditions of sorption experiment are found to play a major role. As pH decreases, percentage of extraction is found to be increasing (Vide Graph: B: 1). As for example, with the leaves powders of Justicia adhatoda, % of extractability is found to be : 36.0% at pH: 10, 44.0% at pH: 8, 52.0% at pH: 6, 72.0% at pH: 4 and 88.0% at pH: 2 after an equilibration time of 2.5 hrs with sorbent concentration of 2.5 gm/500 ml. With the leaves powders of *Cissus quadrangularis*, % of extractability is found to be 16.0 % at pH:10, 20.0% at pH:8, 28.0% at pH:6, 48.0% at pH:4 and 88.0% at pH: 2 after an equilibration time of 2.0 hrs and with the sorbent concentration of 2.5 gm/500 ml . In the case of leaves powders of Soapnut Acacia, % of extractability is found to be 20.0% at pH:10, 24.0% at pH:8, 36.0% at pH:6, 76.0% at pH:4 and 84.0 % at pH:2 after an equilibration time of 2.0 hrs and sorbent concentration of 2.0 gm/ 500 ml.

4. **Sorbent Concentration**: The sorbent dosage needed for the maximum extraction of Chromate at pH: 2 and at optimum equilibration times is found to be 2.5 gram/500 ml for the leaves powders of Justicia adhatoda; 2.5 gm/500 ml for leaves powders of *Cissus quadrangularis* ; 2.0 gm/ 500 ml for leaves powders of Soapnut Acacia (vide Graph No.: C:1)

5. The % of maximum extractability of Chromium (VI) at optimum conditions of pH and equilibration time are found to be 88.0%, 88.0% and 84.0% in the case of leaves powders of Justicia adhatoda, *Cissus quadrangularis*, Soapnut Acacia respectively (vide Graph Nos.A:1-3).

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

- **Cations:**

It is interesting to note that the extractability is markedly enhanced in presence of. cations ions. The tenfold excess of Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} ions, is found to increase the % of exctraction of Chromium respectively from 88.0% to 100.0%, 94.3%, 97.8% ,96.1%, 97.9% and 99.1 % respectively with the leaves powders of *Justicia adhatoda* (vide Table No.: 1:column No.3) ; from 88.0% to 99.3%, 93.8%, 97.2% 95.5%, 97.2% and 98.4% respectively with the leaves powders of *Cissus quadrangularis* (vide Table No:1: Column No. 4)); and from 84.0% to 95.7% , 88.7% , 92.3 % , 91.6%, 92.4% and 94.8% respectively with leaves powders of *Soapnut Acacia* (vide Table No. 1: Colum No.5).

Further, it is interesting to note that the extent of interference is found to be in the expected order:

$$\mathbf{Ca^{2+} > Fe^{2+} > Ni^{2+} \sim Cu^{2+} > Zn^{2+} > Mg^{2+}} .$$

- **Anions:**
- **Phosphate, Sulphate and Carbonate** are found to be interfering and the extent of interference is found to be in the order: $PO_4^{3-} > SO_4^{2-} > CO_3^{2-}$.

- **Ten fold excess of $\mathbf{PO_4^{3-}}$** is found to reduce % of extraction from 88.0% to 62.3% in the case of leaves of Justicia adhatoda; 88.0% to 61.2% with leaves powder of *Cissus quadrangularis* ; 84.0 % to 60.9 % with leaves powder of SoapnutAcacia (vide S. No. 5 of Table Nos:1)

- Tenfold excess of SO_4^{2-} is found effect the % extraction from 88.0% to 64.4 % in the case of powder of leaves of *Justicia adhatoda* as sorbent; 88.0% to 63.6% with leaves powder of *Cissus quadrangularis*; 84.0 % to 62.9 % with leaves powder of Soapnut Acacia (vide S. No. 2 of Table Nos:1).

- **CO_3^{2-}** in tenfold excess, is also found to decrease the % of extraction from 88.0% to 71.9% in the case of powder of leaves of *Justicia adhatoda*; 88.0% to 71.1% with leaves powder of ***Cissus quadrangularis***; 84.0 % to 70.2 % with leaves powder of *Soapnut Acacia* (vide S. No. 7 of Table Nos:1).
- Ten fold excess of Nitrate , Chloride and Fluoride and are found to have marginal interference with the % of extractability of Chromium in all the sorbents of interest (vide Sl. Nos. 3,4&6 of Table No. 1).Even then, the natural expected order of interference: $NO_3^- > Cl^- > F^-$ is followed.

DISCUSSION

The available data is in adequate in understanding the sorption characteristics of the adsorbents. A thoroughly surface morphological study adopting such modern techniques like X-ray Photo Electron Spectroscopy (XPS), Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrum (EDS) techniques are needed in addition to the classical elemental chemical analysis before and after the sorption of the adsorbate on the sorbent surface. It beyond the scope of their work.

However, the observations may be accounted as follows:

- The bio-sorbents may be having some natural compounds, which have affinity towards Chromate at low pH values.
- The functional groups present in the lingo celluloses' materials like leaves are -OH/-COOH and dissociation of these groups are pH sensitive. At high pHs, the surfaces are charged with negative charge and hence, the surfaces have thrust for cations while at low pHs, the surfaces may have positive charge due to protination, and hence show affinity towards weak anions . The dissociation of the functional groups may be represented as:
-

At high pH values: $\text{Adsorbent-OH} \rightleftharpoons \text{Adsorbent-O}^- + H^+$

$\text{Adsorbent-COOH} \rightleftharpoons \text{Adsorbent-COO}^- + H^+$

At low pH values: $\text{Adsorbent-OH} + H^+ \rightleftharpoons \text{Adsorbent-}\underset{H}{O^+}H$

In basic solutions, the hexavalent Chromium presents as tetrahedral Chromate ions CrO_4^{2-}; between pH: 2 to 6, the species: $HCrO_4^-$ and the orange red dichromate ions $Cr_2O_7^{2-}$ are in equilibrium; and at pH values less than 1, the main species is H_2CrO_4.

So, Chromate being an anion in the pH range: 2-6, is sorbed to the leaves materials at low pHs due to weak anion exchange nature and thus results in higher % of removal at low pH values. As pH increases, the cation exchanging nature prevails and this results in low % removal of Chromate ions.

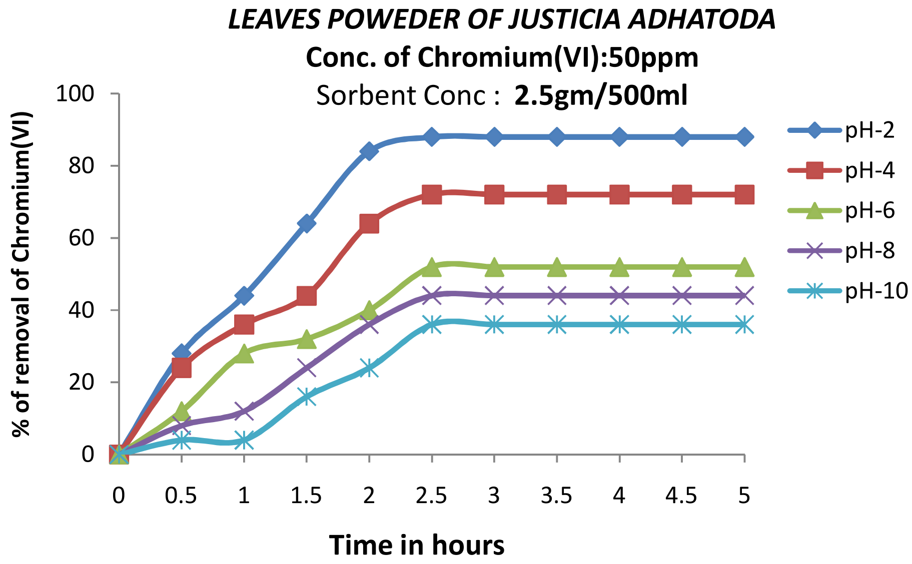
- Further, biomaterials may contain some impurities of metal ions like Mg, Ca, Fe, Al. which form sparingly soluble salts with Chromate. These precipitates are gelatinous in nature and are being trapped in the matrixes of the bio-adsorbents removal of Chromate.
- The decrease in the rate of adsorption 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 thus resulting in decrease in capability of the adsorbent.
- The observations made with respect to the foreign ions are also conforming as per the expected nature of extraction. PO_4^{3-}, SO_4^{2-} and CO_3^{2-} are found to effect the percentage of extractability in the order: $PO_4^{3-} > SO_4^{2-} > CO_3^{2-}$ while F^-, Cl^- and NO_3^- have marginal effect. In the case of Cations, the % extraction of Chromium(VI) is increased. This kind of synergic effect may be due to the formation of sparingly soluble gelatinous precipitates of metal chromates, which are trapped or occulted in the matrix of the sorbents.

Applications:

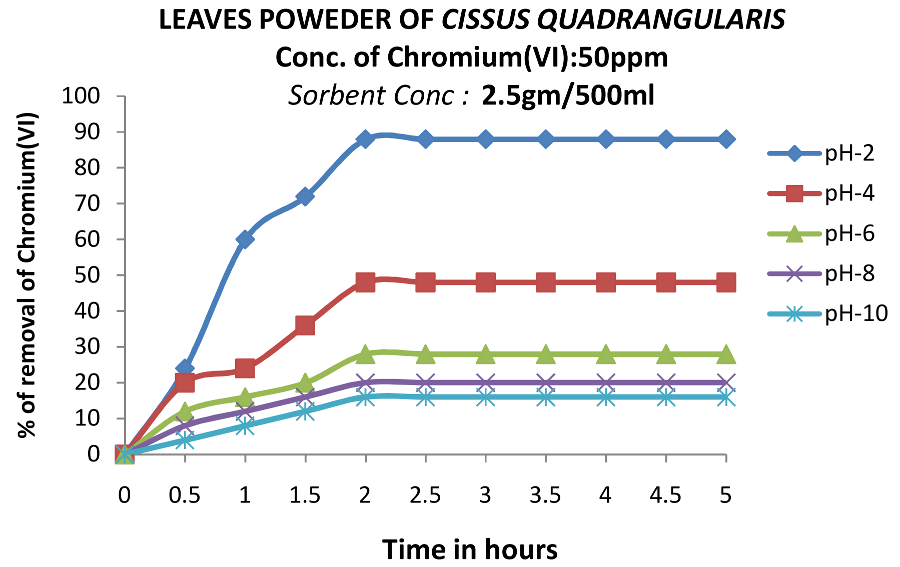
The methodologies developed in this work were applied to the real samples of diverse nature, which were collected from the sewages/effluents of Tannery and Chrome plating industries and in polluted lakes (fed with known amounts of hexavalent Chromium). The results have been presented in the Table No: 2.

It is found that the sorbents developed in this work are remarkably successful in removing Chromium(VI) in all the samples studied at optimum conditions of pH, equilibration time and sorbent dosage as given in the Table 2 . Percentage removal of Chromium(VI) is found to be: 79.5% to 84.5% with leaves powder of *Justicia adhatoda* ;

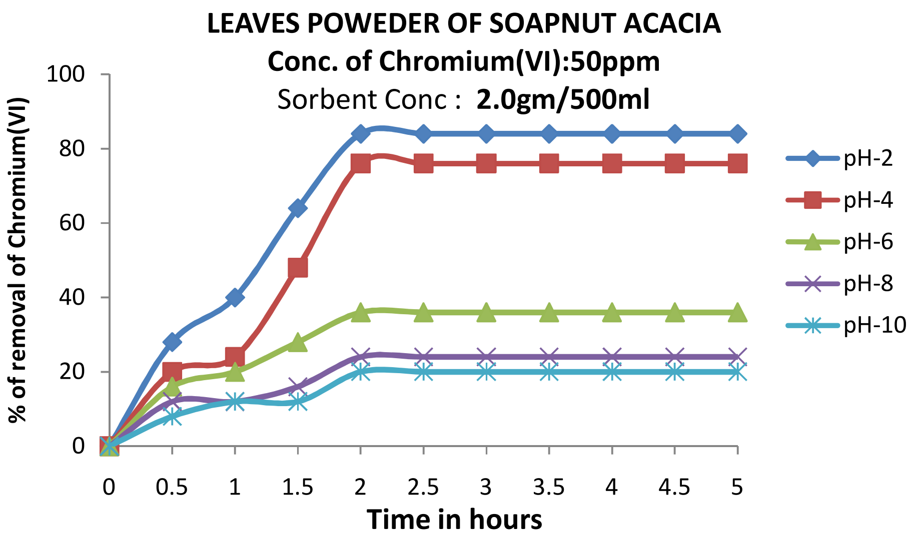
78.0% to 83.3% with leaves powders of *Cissus quadrangularis*; 77.5% to 82.5% with leaves powders of Soapnut Acacia (vide Table No.2).



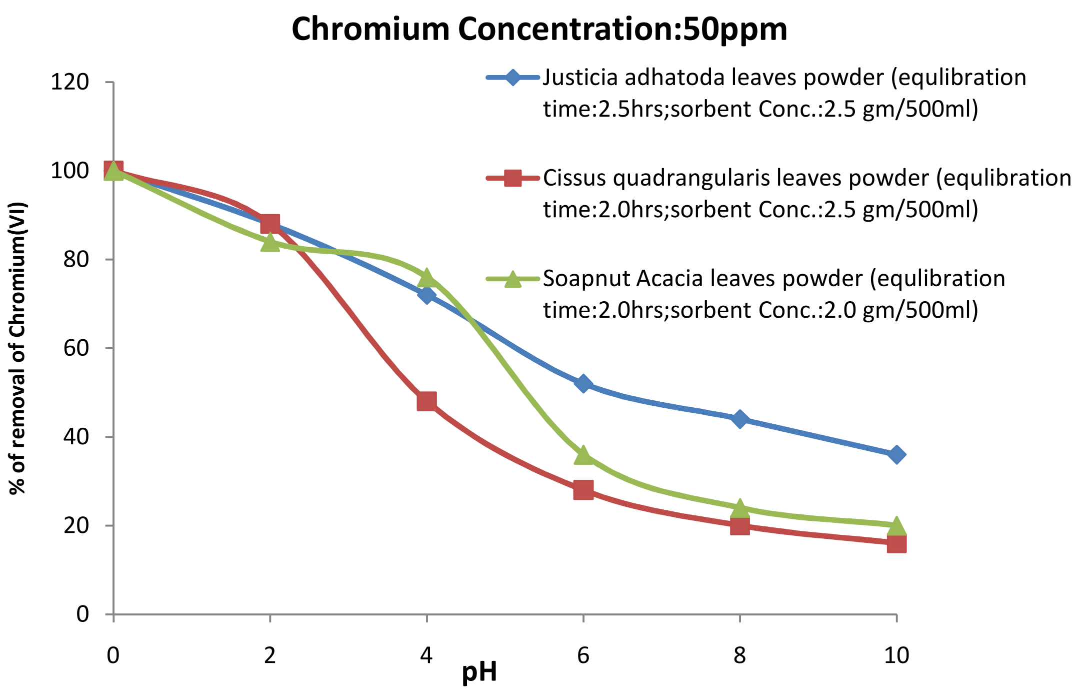
Graph No. : A:1:Time Vs % of removal of Chromium(VI)



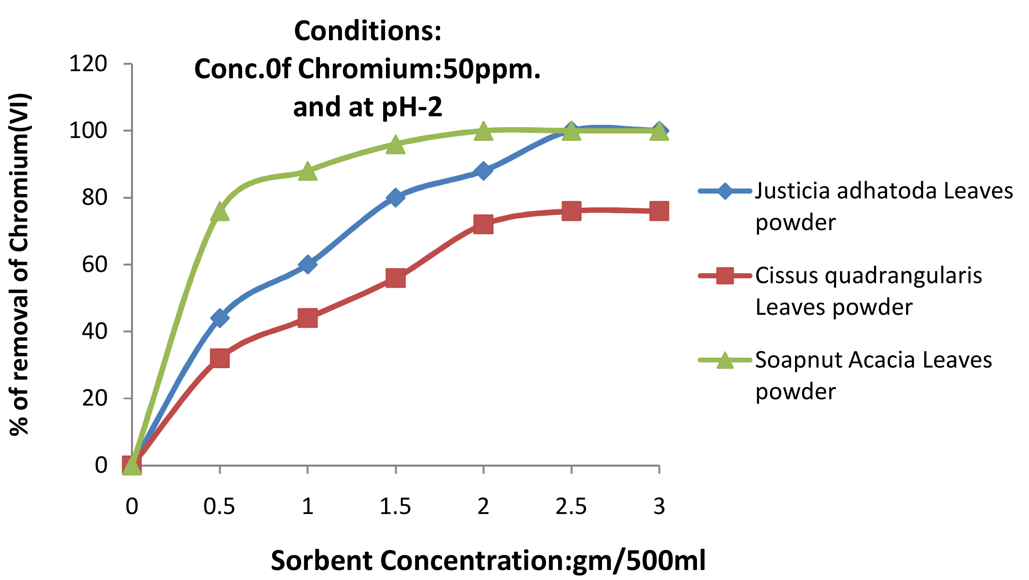
Graph No. : A:2:Time Vs % of removal of Chromium(VI)



Graph No. : A:3:Time Vs % of removal of Chromium(VI)



Graph No.:B:1: pH Vs % of removal of Chromium(VI):50ppm



Graph No. :C:1: Sorbent Concentration Vs % of removal of Chromium(VI)

Table No: 1: Effect of interfering Ions on the Extractability of Chromates with different Bio-sorbents:

Sl..No	*Interfering ions : Ten fold excess*	*% of maximum extractability in synthetic water samples containing 50.0 ppm of Chromium (VI)*		
		Justicia adhatoda leaves Powder :mesh:75 µ *pH:2* *Equilibration time:2.5 hrs;* *Sorbent Conc.: 2.5 gms/500 ml*	*Cissus quadrangularis leaves Powder: mesh:75 µ* *pH:2* *Equilibration time: 2.0 hrs;* *Sorbent Conc.: 2.5 gms/500 ml*	*Soapnut Acacia leaves powder :mesh:75 µ* *pH:2* *Equilibration time: 2.0 hrs;* *Sorbent Conc.: 2.0gms/500 ml*
1.	*Without interfering ions*:	88.0%;	88.0%	84.0%
2.	SO_4^{2-}	64.4%	63.6%	62.9%
3.	NO_3^-	84.9%	84.2%	80.3%
4.	Cl^-	86.8%	86.1%	82.2%
5.	PO_4^{3-}	62.3%	61.2%	60.9%
6.	F^-	87.4%	87.1%	83.2%
7.	CO_3^{2-}	71.9%	71.1%	70.2%
8.	Ca^{2+}	100.0%	99.3%	95.7%
9.	Mg^{2+}	94.3%	93.8%	88.7%
10.	Cu^{2+}	97.8%	97.2%	92.3%
11.	Zn^{2+}	96.1%	95.5%	91.6%
12.	Ni^{2+}	97.9%	97.2%	92.4%
13.	Fe^{2+}	99.1%	98.4%	94.8%

Table No: 2: Extractability of Chromium (VI) in Different Industrial and Natural Samples using Bio-sorbents

SAMPLES COLLCETED AT DIFFERENT PLACES	Cr(VI) in the Sample	% of Maximum extractability		
		Justicia adhatoda leaves Powder :mesh:75 µ pH:2 Equilibration time:2.5 hrs; Sorbent Conc.: 2.5 gms/500 ml	*Cissus quadrangularis* leaves Powder: mesh:75 µ pH:2; Equilibration time: 2.0 hrs; Sorbent Conc.: 2.5gms/500 ml	Soapnut Acacia leaves powder :mesh:75 µ pH:2; Equilibration time: 2.0 hrs; Sorbent Conc.: 2.0gms/500 ml
Tannery Industry Effluents:				
1	12.5 ppm	83.2%	79.6%	77.5%
2	21.5 ppm	82.0%	78.0%	78.0%
3	14.5 ppm	81.0%	80.5%	80.5%
Chromate Plating Industry Effluents:				
1	21.5 ppm	82.5%	82.5%	78.5%
2	24.5 ppm	79.5%	83.3%	79.5%
3	15.8 ppm	80.8%	78.5%	81.5%
Natural Lake Samples(fed with known amounts of Chromates):				
1	15.0 ppm	83.1%	79.5%	81.0%
2	20.0 ppm	84.5%	78.5%	82.5%
3	25.0 ppm	83.9%	81.0%	82.0%

CONCUSSION

1. Leaves Powder of *Justicia adhatoda* , *Cissus quadrangularis*, Soapnut Acacia are found to have strong affinity towards Chromium(VI) ions at low pH values.
2. % of removal of Chromate is pH sensitive and also depends on sorption concentration and time of equilibration.
3. The conditions for the maximum extraction of Chromium(VI) at minimum sorbent concentration and equilibration time have been optimized.
4. Ten fold excess of common cation ions present in natural waters, viz., Ca^{2+}, Mg^{2+},Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+}, have synergistic effect in increasing the % removal of Chromium(VI). SO_4^{2-}, PO_4^{3-} and CO_3^{2-} are found to be interfering with the extractability of Chromium(VI) in the order: $PO_4^{3-} > SO_4^{2-} > CO_3^{2-}$. The other anions: NO_3^- , Cl^- and F^- and are found to have marginal interference.
5. We claim 88.0%, 88.0%, and 84.0% of removal of Chromium(VI) from synthetic waters with the leaves powders of *Justicia adhatoda* , *Cissus quadrangularis*, Soapnut Acacia respectively at pH:2 and at optimum equilibration time and sorbent concentrations.
6. The methodologies developed in this work are found to be remarkably successful in removing the Chromium(VI) from industrial effluents and polluted lake samples as detailed in Table No: 2.

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