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Extraction of hexavalent chromium from polluted waters using bio-adsorbents derived from leaves of *Croton tiglium* and *Cassia occidentalis* plants

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ABSTRACT

The adsorption abilities of bio-sorbents derived from plant materials towards polluting ions is one of the highly thrust areas of pollution control research and is being intensively probed in developing simple, efficient and eco-friendly methodologies in the removal of hazardous ions. In the present work, bio-adsorbents derived from leaves of *Croton tiglium* and *Cassia occidentalis*, have been investigated for their adsorption nature towards Chromium (VI) ions. The effects of various physicochemical parameters viz., equilibration time, pH and sorbent concentration, on the extraction of Chromium (VI) have been studied and optimized. Common cation ions (in tenfold excess) normally present in natural waters, viz., Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} and Fe^{2+} are found to have synergistic effect in increasing the % removal of Chromium. Anions like Phosphate, SO_4^{2-} and Carbonate are found to be interfering in the order: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. The monovalent ions: NO_3^- , Chloride, and Fluoride are found to have marginal interference. More than 90.0% extraction of Chromium (VI) is observed with the developed active sorbents. The methodologies developed are applied to real samples of industrial effluents and polluted lakes and found to be remarkably successful.

Key words: Chromium (VI), pollution control, bio-sorbents, *Croton tiglium*, *Cassia occidentalis*

INTRODUCTION

Chromium salts are highly toxic [1-3] and are used widely in various industries such as a tanning, metallurgical, paints, inks, wood preservatives, rubber, ceramics, fungicides, photography and textile [1-5]. The effluents of these industries cause environmental pollution if effluents are not adequately treated for the removal of Chromium and proper scientific methods of disposal methods are not adopted. This results in the entry of non-degradable Chromium (VI) into the water bodies causing potential threat to the aquatic life, more so by the process of bio-amplification and gets accumulated to food chain in unspecific compounds inside the cells of living organisms causing toxicity at cellular level [3-6].

Of the two states of Chromium, hexavalent ion is many folds toxic than trivalent ion. It is attributed to higher oxidation potential of Chromium (VI) [6] which causes easily penetration in to biological membranes, resulting health hazards [6] such as irritation, corrosion of skin, respiratory track and lung carcinoma and acute tubular

necrosis of the kidney and consequent death [2,3,6]. Potable limit of Chromium is $0.05 \mu\text{g/ml}$ [2,3&6]. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is: $100 \mu\text{g/ml}$ and US EPA primary drinking water standard is: $0.1 \mu\text{g/ml}$ of total Chromium [6].

Researchers are trying to evolve methodologies for controlling this potential health hazard [5-37]. Several procedures have been developed, both in field and lab, 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] and bone charcoal [23].

Increasing research interest is seen in using biomaterials derived from plant materials such as leaves, barks, biomasses, and agricultural wastes in controlling the pollution. Our research group has been investigating on these bio-methods of pollution and developed methods for the removal of Chromium (VI) (38-41), Zinc (42,43), Aluminum (III) (44-47), Fluoride (48-54), Nitrite (55,56), Nitrates (57), Ammonia (58-60), Phosphate (61,62) and Dyes (63-66) and some heavy metal ions (67). These methods offer a potential alternative to the existing methods of detoxification and the recovery of toxic and valuable ions from industrial discharges/ polluted waters. So far the methods aimed to remove Chromium from polluted waters based on bio-approaches [28, 30-41], though have achieved some degree of success, universally acceptable, simple, effective and economical method is still eluding the researchers.

The present work aims to explore the sorption abilities of biomaterials derived from the leaves of some herbal plants in effecting the Chromium (VI) removal from polluted waters.

MATERIALS AND METHODS

All chemicals used were of analytical grade. 50.0 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.

(A) Adsorbents:

Of the various plant materials probed for their sorption properties, powders of leaves of *Croton tiglium* and *Cassia occidentalis*, have been found to have affinity towards the Chromium (VI) ions.



Croton tiglium

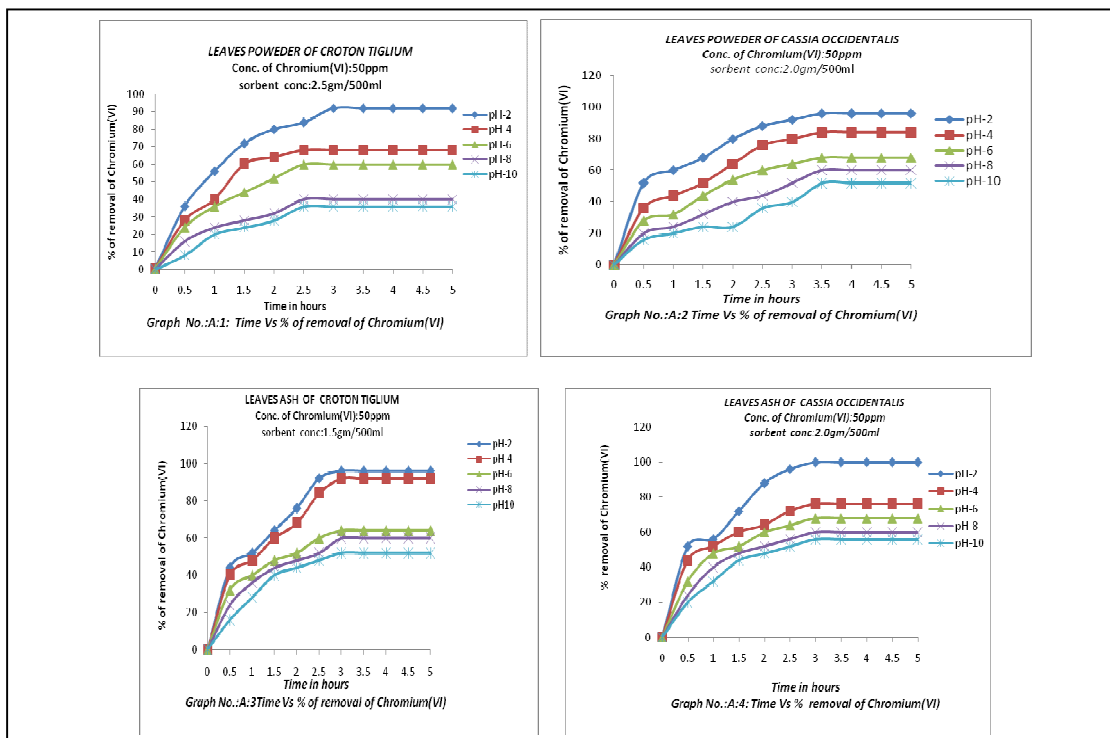


Cassia occidentalis

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

Croton tiglium is an herbal plant, indigenous to South Asian Countries and belongs to Euphorbiaceae family. It is one of the fifty fundamental herbs used in traditional Ceylon and Chinese medicines. *Cassia occidentalis* is an erect, annual herb and it belongs to Fabaceae family and is grown throughout India even up to an altitude of 1,500 meters. The leaves and shell of it are used in Ayurvedic and Unani systems of medicines as infusion. The extracts of materials of this plant show positive response on guinea pig-ileum, rat-uterus, rabbit-heart, and a depressor-effect on the blood-pressure of dogs and are widely used in house hold preparations for the treatment of distention of stomach, hiccups, vomiting and biliousness

The leaves of *Croton tiglium* and *Cassia occidentalis* 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: $<75\mu$ and activated at 105°C in an oven and then employed in this study. Further, the dried leaves were burnt to ashes and these ashes were also used in this work.



(B) 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 were 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 [68].

Estimation of Chromium (VI): An aliquot amount of Chromate sample was taken in a 50ml 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 biomaterials were studied with respect to the time of equilibration, pH and sorbent dosage. At a fixed sorbent concentration, the % removal of Chromate was studied with respect to time of equilibration at various pH values. The results obtained were presented in the Graph Nos. A: 1-4 and B: 1. To fix the minimum dosage needed for the maximum removal of the Chromate ions for a particular sorbent, at optimum pH and equilibration times, extraction studies were made by studying the % of extraction with respect to the sorbent dosage. The results obtained were presented in the Graph Nos. C: 1.

(C) Effect of Interfering Ions:

The interfering ions chosen for study are the common ions present in natural waters, viz., Sulphate, Nitrate, Chloride, Phosphate, Fluorides, Carbonate, Calcium, Magnesium, Copper, Zinc, Nickel and Iron ions. The synthetic mixtures of Chromium (VI) and one of the interfering ions were so made that the concentration of the interfering ions 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 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). % of extraction was calculated from the data obtained. The results are presented in the Table No. 1.

(D) Applications of the developed bio-sorbents:

The adoptability of the procedures developed in this work for the removal of Chromium (VI) is tested with some real sewage/effluent samples of some industries and polluted lakes. For this purpose, three samples were collected from tannery industries in Hyderabad and three from Chrome plating industries in Chennai and these samples were analyzed for the actual concentration of Chromium (VI). Further, three more natural samples from three lakes at different places in Bapatla mandalam of Guntur Dt of Andhra Pradesh were collected and these sample were fed with known amounts of Chromium (VI) as given in the Table No.2.

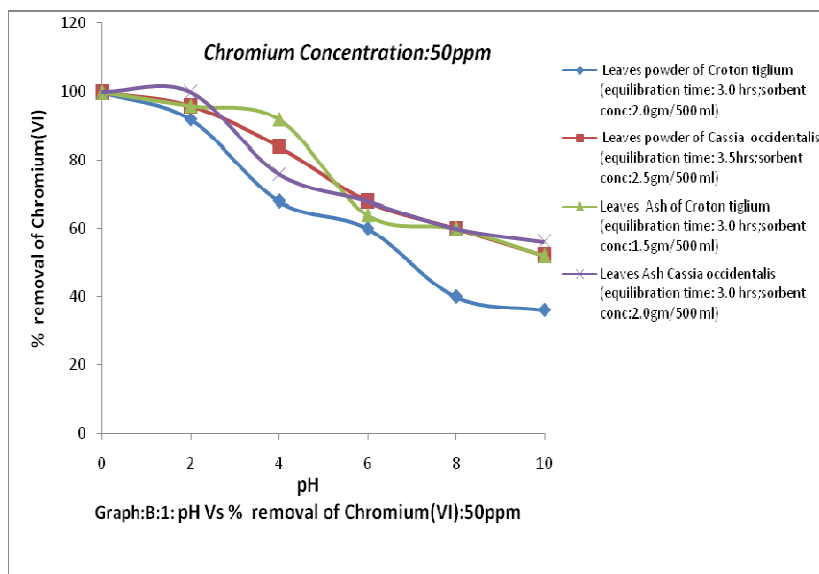
Then these samples were *subjected to extraction for Chromium (VI) using the bio-sorbents developed in this work at optimum conditions of pH, equilibration time and sorbent concentration. The results obtained were presented in the Table No 2.*

RESULTS AND DISCUSSION

The sorption characteristics of thermally activated leaves and their ashes of *Croton tiglium* and *Cassia occidentalis* with respect to various physicochemical parameters are presented in the Graph No. A: 1-4; B: 1 & C: 1 and in Table Nos. 1 & 2. The following observations are significant:

1. **Time of equilibration:** % of extractability increases with time for a fixed sorbent and at fixed pH and after certain time, the extractability remains constant i.e. an equilibrium state has been reached (Graph Nos. A: 1-4). In other words, there will not be any further adsorption after certain time of equilibration time. As for example, in the case of thermally activated leaves powders of *Croton tiglium*, % of extraction is 36.0% at 0.5 hrs, 56.0% at 1.0 hr, 72.0% at 1.5 hrs, 80.0% at 2.0 hrs, 84.0% at 2.5 hrs, 92.0% at 3.0 hrs, 92.0% at 3.5 hrs and 92.0% above 4.0 hrs. as pH:2 and at Sorption concentration 2.0 gm/500 ml (vide Graph No.A:1). The same trend is noticed in the case of other sorbents.

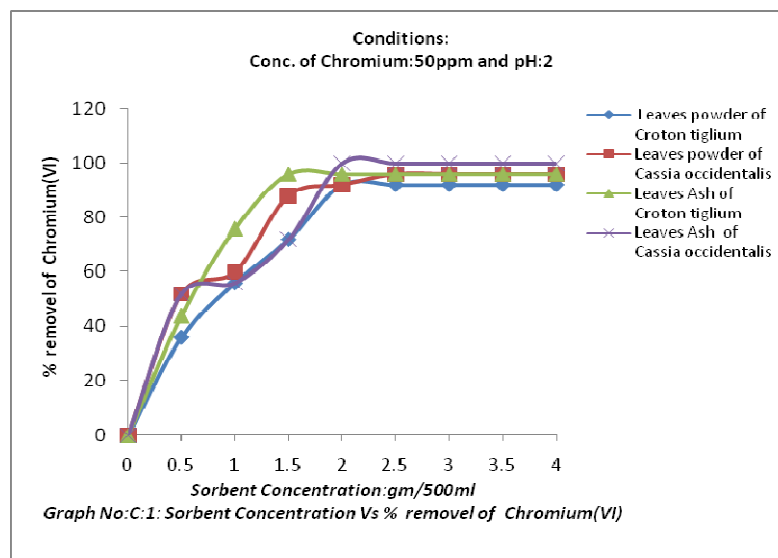
2. **pH effect:** % of extraction is found to be pH sensitive. % of extraction of Chromium(VI) is found to be increasing with decrease in pH (Vide Graph: B: 1). As for example, with the thermally activated powders of *Croton tiglium*, % of extractability is found to be 36.0% at pH: 10, 40.0% at pH: 8, 60.0% at pH: 6, 68.0% at pH: 4 and 92.0% at pH: 2 after an equilibration time of 3.0 hrs and with sorption concentration of 2.0 gm/500 ml. In the case of ashes of *Croton tiglium*, the extraction of Chromium (VI) is found to be 52.0% at pH: 10, 60.0% at pH: 8, 64.0% at pH:6, 92.0% at pH:4 and 96.0% at pH:2 after an equilibration time of 3.0 hrs and with sorption dosage of 1.5 gms/500 ml. Similarly, with the leaves powders of *Cassia occidentalis*, % of extractability is found to be 52.0 % at pH:10, 60.0% at pH:8, 68.0% at pH:6, 84.0% at pH:4 and 96.0% at pH: 2 after an equilibration time of 3.5 hrs with sorbent concentration of 2.5 gm/500 ml while with the ashes of *Cassia occidentalis*, % of extractability is found to be: 56.0% at pH:10, 60.0% at pH:8, 68.0% at pH:6, 76.0% at pH:4 and 100.0 % at pH:2 after an equilibration time of 3.0 hrs with the sorbent dosage of 2.0 gm/500 ml.



3. **The maximum % of extractability** is found to be more with ashes of leaves than with the corresponding leaves powders. With leaves powders of *Croton tiglium*, % of maximum removal of Chromium (VI) is found to be 92.0% and with their ashes : 96.0% at the optimum conditions of extraction. In the case of leaves powder of *Cassia occidentalis*, % of removal is 96.0% while with its ashes 100.0% at optimum conditions pH and sorbent concentration (Vide Graph No.A:1-4 and Table No.1: Sl. No.1)

4. **Time of equilibration** needed for maximum extractability of Chromate is found to be less for the ashes of leaves of *Cassia occidentalis*, 3.0 hrs, than with the thermally activated raw leaves powder, 3.5 hrs. In the case of *Croton tiglium*, the optimum time of equilibration is 3.0 hrs for both ash and raw leaves.

5. **Sorbent Concentration:** The optimum sorbent dosage for the maximum extraction of Chromium (VI) is found to be less in the case of ashes of leaves than with raw powders.



Optimum sorbent dosage is found to be 2.5g/500 ml for the leaves powder of *Cassia occidentalis* while with its ashes 2.0 g/500 ml. Similarly, with the leaves powders of *Croton tiglium*, optimum sorbent dosage is found to be 2.0g/500ml while with their ashes 1.5 gm/500 ml (Vide Graph No. C: 1).

6. The % of maximum extractability of Chromium (VI) at optimum conditions of pH and equilibration time are found to be: 92.0% with *Croton tiglium* leaves powder and 96.0% with its ashes; 96.0% with *Cassia occidentalis* leaves powder and 100.0% with its ashes (vide Graph Nos.A:1-4; Table No.1: Sl. No. 1).

7. **Interfering Ions:** The extractions of Chromium (VI) ions in presence of ten fold 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.

Table No: 1: Effect of interfering Ions on the Extractability of Chromates with different Bio-sorbents					
S.No	Interfering ions : Ten fold excess	% of maximum extractability in synthetic water samples containing 50.0 ppm of Chromium (VI)			
		Leaves of <i>Croton tiglium</i>		Leaves of <i>Cassia occidentalis</i>	
		Thermally activated powders (mesh:75 μ) :pH:2;3.0 hrs & 2.0 gms/500 ml	Ashes pH:2;3.0 hrs & 1.5 gms/500 ml	Thermally activated powders (mesh:75 μ) pH:2;3.5 hrs & 2.5 gms/500ml	Ashes pH:2;3.0 hrs & 2.0 gms/500 ml
1.	Without interfering ions:	92.0%;	96.0%	96.0%	100.0 %
2.	SO_4^{2-}	68.0 %	72.1%	65.3%	72.9%
3.	NO_3^-	88.5%	96.0%	92.8%	96.8%
4.	Cl^-	91.3%	92.2%	96.0%	100.0%
5.	PO_4^{3-}	64.5%	68.0%	62.9%	64.9%
6.	F^-	91.7%	94.9%	92.3%	96.8%
7.	CO_3^{2-}	80.6%	84.3%	80.9%	92.9%
8.	Ca^{2+}	92.5%	100%	96.2%	100.0%
9.	Mg^{2+}	100.0%	97.3%	98.9%	100.0%
10.	Cu^{2+}	97.8%	98.7%	97.3%	100.0%
11.	Zn^{2+}	98.3%	98.1%	100.0%	100.0%
12.	Ni^{2+}	96.1%	96.3%	96.9%	100.0%
13.	Fe^{2+}	97.5%	100.0%	96.3%	100.0%

It is interesting to note that in the presence of tenfold excess of cations chosen for study, the % removal of Chromium (VI) is enhanced. As for example, with the thermally active leaves powder of *Croton tiglium*, the % of extraction of Chromium (VI) :92.0% (in the absence of foreign cations), is enhanced to 92.5%, 100.0%, 97.8%, 98.3, 96.1 and 97.5% in presence of Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} and Fe^{2+} ions respectively. The same trend is found in the case of other sorbents (Vide Table No.1: Sl. No. 8 to 13). This kind synergetic effect in enhancing the % removal of Chromium (VI) is phenomenal and needs further probe.

In the case of anions, PO_4^{3-} , SO_4^{2-} and CO_3^{2-} are found to be interfering. The extent of interference is found to be in the order: $PO_4^{3-} > SO_4^{2-} > CO_3^{2-}$. As for example % of extraction is decreased from 92.0% to 64.5% in presence of PO_4^{3-} , 68.0% in presence of SO_4^{2-} and 80.6% in presence of CO_3^{2-} , in the case of thermally activated leaves powder of *Croton tiglium* as adsorbent (Vide Table No. 1: Sl. No.1, 2, 5 &7). The same trend is found with other sorbents of interest (Vide Table No. 1: Sl. No.1, 2, 5 &7).

Ten fold excess of other anions viz., NO_3^- , Cl^- & F^- are found to marginal interference with the % of extractability of Chromate in all the sorbents of interest (vide Sl.Nos. 3,4 &6 of Table No. 1).

DISCUSSION

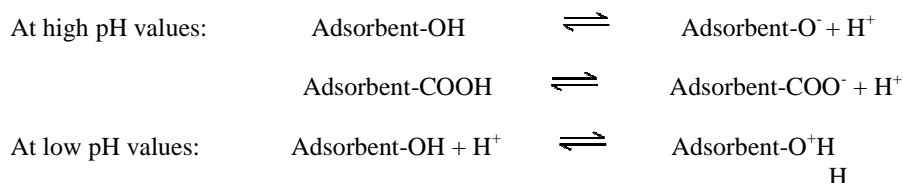
With the available data, it is not possible to account theoretically each observation as it needs studies on the surface morphology to understand the sorption chemistry using such modern techniques like X-ray Photo Electron Spectroscopy (XPS), Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrum (EDS) in addition to the classical elemental chemical analysis before and after the sorption of the Chromium (VI) on the sorbent surface. It beyond the scope of this work.

However, the observations may be accounted as follows:

1. The bio-sorbents may be having some natural compounds, which have affinity towards Chromate at low pH values.

2. 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 shows affinity towards weak anions. The dissociation of the functional groups may be represented as:

3.



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 $\text{Cr}_2\text{O}_7^{2-}$ 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.

4. Further, these natural materials may have traces of divalent and trivalent metal ions that form sparingly soluble salts with Chromate and these precipitates are gelatinous in nature and are being trapped in the matrixes of the bio-adsorbents and thus resulting in the increase of % removal of Chromate. This is more so in the case of ashes as adsorbents, which are oxides of some metal ions.

5. Ashes are the oxides of some heavy metals containing large amounts of silica. These ashes, contains '-OH' and '-O-' groups. The observed behaviors of increase in extractability with the decrease in pH may be understood in the same lines as described in the case of raw powders of leaves. In fact, the transition pH for silica from anion exchanging nature to cation exchanging nature is 3 [69-71] and this supports the proposed logic for the observed behavior.

6. 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.

7. The observations made with respect to the foreign ions are as per the expected nature of extraction. Percentage of extractability is affected in the presence anions: phosphates Sulphate and Carbonates and the extent of interference is of the order $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. Monovalent anions F^- , Cl^- & NO_3^- are not interfering with the extraction of Chromium (VI). 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.

Table No: 2: Extractability of Chromium (VI) in Different Industrial and Natural Samples using Bio-sorbents					
Samples collected at different places	Cr(VI) in the Sample	% of Maximum extractability			
		Leaves of <i>Croton tiglium</i>		<i>Cassia occidentalis</i>	
		Thermally activated Powders (mesh:75 μ):pH:2;3.0 hrs & 2.0 gms/500ml	Ashes pH:2;3.0 hrs & 1.5 gms/500ml	Thermally activated powders (mesh:75 μ) pH:2;3.5 hrs & 2.5 gms/500 ml	Ashes pH:2;3.0 hrs & 2.0 gms/500 ml
<i>Tannery Industry Effluents</i>					
1	16.5 ppm	80.6%	85.3%	74.6%	78.5%
2	23.5 ppm	78.3%	87.8%	79.6%	79.5%
3	15.5 ppm	84.1%	91.2%	81.3%	76.5%
<i>Chromate Plating Industry Effluents</i>					
1	20.5 ppm	82.3%	87.4%	92.5%	82.9%
2	24.5 ppm	85.1%	82.4%	88.5%	86.6%
3	17.8 ppm	87.8%	85.8%	86.5%	88.7%
<i>Natural Lake Samples(fed with known amounts of Chromates):</i>					
1	14.0 ppm	89.5%	91.2%	87.5%	92.5%
2	18.0 ppm	87.5%	90.3%	84.5%	93.6%
3	21.0 ppm	90.5%	93.0%	90.0%	90.6%

4: APPLICATIONS

The Applicability of the methodologies developed in this work were tested with respect to the real samples of diverse nature, which were collected from the sewages/effluents of Tannery and Chrome plating industries and also 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. % removal of Chromium (VI) is found to be: 78.3% to 90.5% with thermally activated leaves powder of Croton tiglium and 82.4% to 93.0% with their ashes; 74.6% to 92.5% with thermally activated leaves powder of Cassia occidentalis and 76.5% to 93.6% with their ashes (*vide Table No.2*).

CONCLUSION

1. Leaves powders and their ashes of *Croton tiglium* and *Cassia occidentalis* have been found to have strong affinity towards Chromate at low pH values.
2. Physicochemical parameters such as pH, sorption concentration and time of equilibration have been optimized for the maximum extraction of Chromium (VI)
3. The conditions for the maximum extraction of Chromate at minimum dosage 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.
5. Phosphate, SO_4^{2-} and Carbonate are found to interfering with the extractability of Chromates in the order: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. Monovalent ions: NO_3^- , Chloride, and Fluoride are found to have marginal interference.
6. We claim 92.0% and 96.0% of extraction of Chromium (VI) respectively using leaves powder of Croton tiglium and their ashes; 96.0% and 100.0 % with the leaves powder of Cassia occidentalis and their ashes.
7. The methodologies developed in this work are tested with respect to diverse waste water samples collected in nine different places. The developed methods have been 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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