

Removal of chromium (VI) from polluted waters using powders of leaves or their ashes of some herbal plants

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Abstract

An investigation is made to explore the surface sorption abilities of powders of leaves and their ashes of some herbal plants. *Achyranthes aspera*, *Mentha*, *Embilica officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum* have been found to have strong affinity towards Chromate at low pH values. Physicochemical parameters such as pH, time of equilibration and sorbent concentration have been optimized for the maximum % removal of Chromium (VI) from waste waters. The minimum dosage and equilibration time needed for the maximum removal of Chromate is found to be less for the ashes of leaves than with the raw leaves powders. More than 90% of extractability for Chromium (VI) has been achieved with some of these bio-sorbents. The presence of tenfold excesses of Cations : Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} and Ni^{2+} , marginally effected the % removal of Chromium (VI) while anions: Sulphates, Nitrate, Cl^- , Phosphate and F^- showed some interference with some sorbents. The adoptability of the methodologies developed in this work are tested with respect to diverse waste water samples collected from industrial effluents and in natural lakes and found to be remarkably successful.

Keywords: Removal of Chromium (VI), Bio-sorption, Herbal plants, Applications

INTRODUCTION

The salts of chromium are widely used in industry in a variety of chemical processes. It is used in the metallurgical industries to alloy with iron, nickel and cobalt to impart resistance to corrosion, in electroplating industry to provide clean finishes and in leather industry as a tanning agent [1]. Chromium is also used in paints, pigments, inks, fungicides, wood preservatives, rubber ceramics, photography and textiles. The wide spread utility of Chromium metal and its salts in various industries leads to the problem of accidental contamination of natural waters due to improper disposal methods. It is reported in Literature that more than 1,70,000 tones of Chromium wastes are being discharged to the environment annually as a consequence of industrial manufacturing activities [2]. Due to its high oxidation potential it can easily penetrate biological membranes and cause health hazards [1, 3, 4].

Chromium in waste water exists in two oxidation states viz., Chromium (III) which normally exist in the form of $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_4^-$ and Chromium (VI) which exist in the form of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} depending on the pH of the solutions [5, 6]. Cr (VI) is considered to be highly toxic compared to Cr (III). Each of these oxidation states has different biocidal, medicinal and toxicological properties [6, 7]. At high concentrations, all the compounds of Chromium are detrimental to the health. Chromium (VI) is hazardous to health when its limit in potable water exceeds 0.05mg / L [8, 9]. The target organ for acute systemic toxicity is the Kidney

resulting in acute tubular necrosis of the kidney and subsequent death. Chromium compounds are also reported to produce allergic reaction and dermatitis in some individuals [8, 10].

Various methods such as Chemical Reduction and Precipitation, Flocculation, Ultra filtration, Evaporation and Concentration, Ion-flotation, Electrolysis and Electroplating etc [11-23] have been reported in literature for removal of Chromium from wastewaters; in all these processes, Cr(VI) is first reduced to Cr(III) by using reducing agents and then precipitating Cr(III) as Chromium Hydroxide by the addition of bases. Activated carbon adsorption, reverse osmosis liquid-liquid extraction, Liquid membrane separation, ion-exchange, bio-sorption and chelating resins and reactive polymer methods have been tried [23-25]. Vasanthi M (2004) et. al studied the removal of Cr (VI) by adsorption on fly ash and commercial activated carbon [26]. S.Dahbi (2002) et.al. [27] studied the removal of trivalent Chromium from tannery waste waters using bone-charcoal. K.N. Sheth and Viral M. Soni (2004) studied the removal of Cr (VI) with activated and adsorbent prepared from tobacco stems [28]. Asha Latha Singh reviewed [29] the removal of Chromium from waste water with the help of microbes. Layu Yee Jin et.al studied [30] removal of Chromium using *Ulvabeytensis* biomass in effecting a biotechnological method for the treatment of industrial waste waters.

Malairajan Singanan et. al [31] (2007) studied on the removal of hexavalent Chromium from industrial wastewater by using biomaterials. R.Shyamala (2005) et.al [32] studied comparison of the adsorption potential of Biosorbents: waste tealeaves and rice husk in the removal of Chromium (VI) from waste waters. There are number of patents on the removal of hexa-valent Chromium form polluted waters [33]

In the present work an attempt is made to explore the sorption abilities of powders of leaves and their ashes of some herbal plants in effecting the Chromium (VI) removal from polluted waters.

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METIRIALS AND METHODS

Chemicals: All chemicals used were of analytical grade.

- 1. Stock solution of Chromium (VI)** was prepared by dissolving 0.144g of A.R. Potassium dichromate in double distilled water and is made up to 1 lit. Its concentration is 50ppm. It is suitably diluted as per the need.
- 2. Diphenyl carbazide solution:** 0.25g of Diphenyl carbazide was dissolved in 50% of acetone.
- 3. 6N Sulphuric acid** was prepared.

Adsorbents

Powders of Leaves and their ashes of various herbal plants were tried for the removal of Chromium from synthetically prepared polluted waters by optimizing various physico-chemical parameters viz., pH, conc. of sorbent and time of equilibration. It has been observed that the Leaves of *Achyranthes aspera*, *Mentha*, *Emblca officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum* have affinity towards the Chromium (VI) ions. The methodology herewith presented is only for these bio-adsorbents.



Achyranthes aspera



Mentha



Emblca officinalis



Azadirachta indica



Hibiscus rosa-sinensis



Ocimum sanctum

Achyranthes aspera is a herbal plant belonging to the Amaranthaceae family and is known to have medicinal values and it grows in tropical conditions. *Mentha* is a herbal plant belonging to the Lamiaceae family and is well grown in moist conditions and it possesses medicinal values. *Emblca officinalis* is one of the most celebrated herbs in the Indian traditional medicine system and it belongs to the Euphorbiaceae family and grows well in India. *Azadirachta indica*, or the Neem tree, is an evergreen tree native to Southeast Asia and it belongs to the Meliaceae family. *Hibiscus rosa-sinensis* is an evergreen flowering shrub belonging to the Malvaceae family and is grown throughout the tropics and subtropics. *Ocimum sanctum* is an aromatic plant in the family Lamiaceae. It is known in South Asia as a medicinal plant and has religious sanctity among Hindus.

Adsorption experiment:

The batch system of extraction procedure was adopted [34-36]. Carefully weighed quantities of adsorbents were taken into previously washed 1 liter/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 a 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 the "Diphenyl Carbazide" method [37].

Estimation of Chromium (VI)

An aliquot amount of Chromate sample was taken in a 50ml volumetric flask. To it 1ml of 6N Conc. H₂SO₄ 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 measured against blank at 540 nm using a 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 the concentration of Chromium in unknown solutions.

The sorption characteristics of the said adsorbents 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: 1-12 and B: 1&2. 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 & 2.

Effect of Interfering Ions:

The interfering ions chosen for study are the common ions present in natural waters, viz., Sulphate, Nitrate, Chloride, Phosphate, Fluorides, Chloride, Carbonate, Calcium, Magnesium, Copper, Zinc and Nickel. The synthetic mixtures of Chromium (VI) and one of the interfering ions were so made that the concentration of the interfering ions maintained at *tenfold 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.

Applications of the developed bio-sorbents:

The adoptability of the methodology developed with the new bio-sorbents in this work for removing Chromium (VI) is tried with some real sewage/effluent samples of some industries. 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).

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.

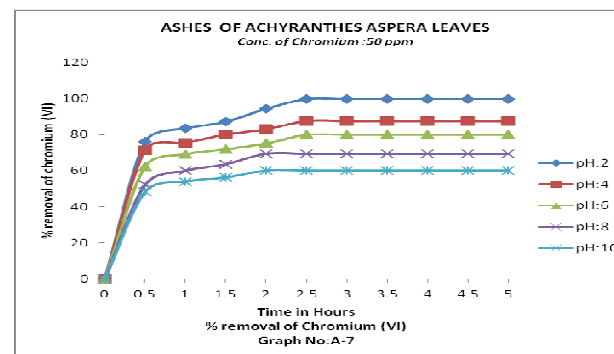
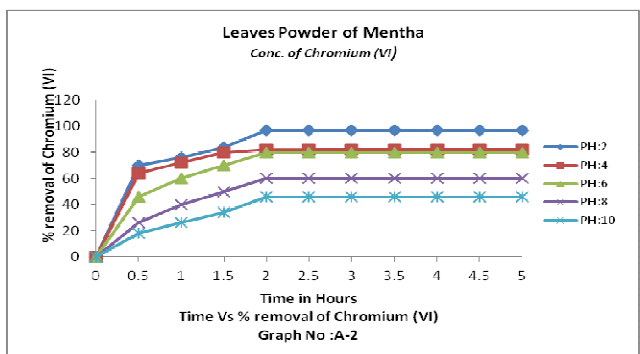
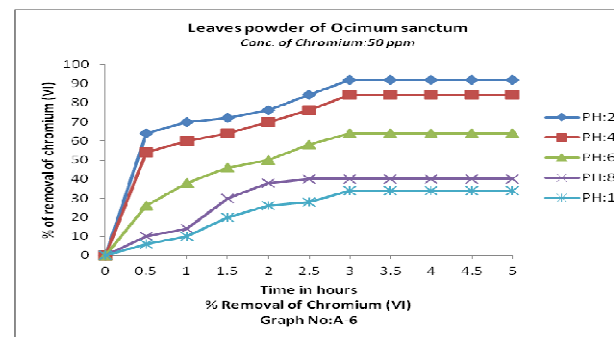
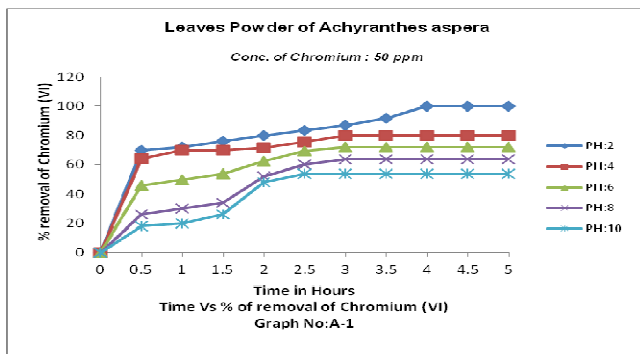
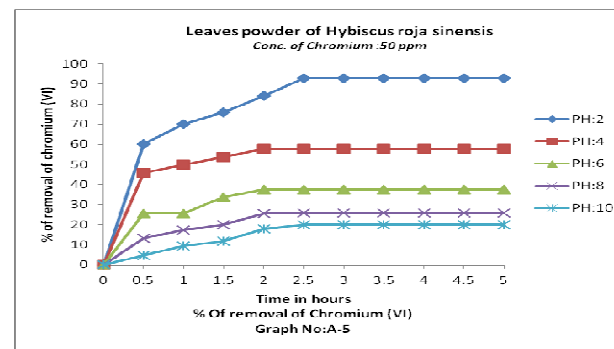
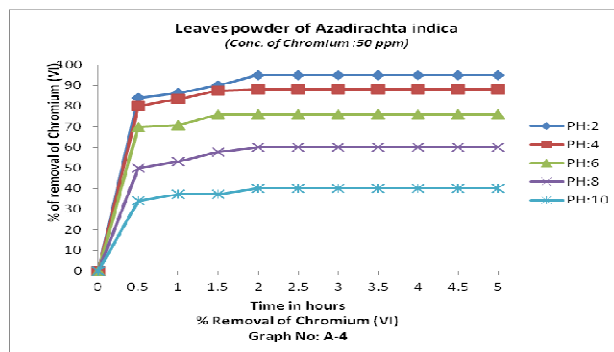
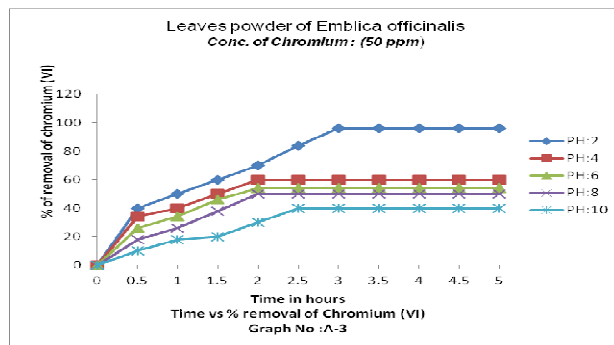
RESULTS AND DISCUSSION

Of the various sorbents tried, the leaves and their ashes of *Achyranthes aspera*, *Mentha*, *Embolica officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum* have been found to have affinity towards *Chromates*. The sorption characteristics of these adsorbents have been studied with respect to various physico-chemical parameters such as pH, time of equilibration and sorption concentration. The results are presented in the Graph No. A: 1-12; B: 1 & 2; C: 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: 1-12).
2. pH: % of extraction is found to be pH sensitive. As pH decreases, % of extraction increases (Vide Graph: B: 1 and 2). As for example, with the powder of leaves of *Achyranthes aspera*, % of extractability, is found to be 54.0% at pH:10; 63.6% at pH:8; 72.0% at pH:6; 80.4% at pH:4 and 97.1% at pH: 2. In the case of ashes of *Azadirachta indica*, the extraction of Chromium (VI) is found to be 26.0% at pH:10, 34.0% at pH:8, 40.0% at pH:6, 54.0% at pH:4 and 97.8% at pH:2. The same trend is found in other sorbents also.
3. The maximum % of extractability is found to be marginally more with ashes of leaves than with raw powders of leaves. As for example, the leaves powders of *Mentha*, the maximum extractability of Chromium (VI) is found to be 96.8% while with their ashes 98.8%; 92.0% with Leaves powder of *Ocimum sanctum* while with their ashes 96.2%; 93.0% with *Hybiscus roja sinensis* leaves powder while 95.0% with their ashes; 96.0% with *Embolica officinalis* leaves powder while 97.0% with their ashes; and 95.0% with leaves powder of *Azadirachta indica* while 97.8% with their ashes.
4. Time of equilibration needed for maximum extractability of Chromate is found to be less for ashes than with the raw powder of leaves. With leaves powders of *Achyranthes aspera*, *Mentha*, *Embolica officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum*, the equilibration time needed for maximum extraction is found to be 4 hrs, 2 hrs, 3hr, 2 hrs, 2.5 hrs and 3.0 hrs respectively at optimum pH:2 while with their ashes, the optimum equilibration times are found to be 2.5 hrs, 1.5 hrs, 2.0 hrs, 1.5 hrs, 2.0 hrs and 2.0 hrs. respectively.
5. Sorbent Concentration: The adsorbent dosage needed for maximum extraction of Chromate is found to be less in the case of leaves powders than their ashes as sorbents. Sorbent concentration for maximum extraction at optimum conditions of pH and equilibration is found to be 2.0 gram/lit for the powders of leaves of *Achyranthes aspera* while with its ashes optimum sorption concentration has been reduced to 1.5 gms/lit. Similarly, with the powders of leaves of *Mentha*, optimum sorbent concentration is 2.5 gm/lit but with their ashes, 2.0 gm/lit is sufficient. In the case of powders of leaves of *Embolica officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum*, the sorbent concentration needed is found to be 2.5 gms/lit, 2.0 gms/Lit, 2.5 gms/lit and 2.0 gms/lit respectively while with their ashes 2.0 gms/lit, 1.5 gm/lit, 2.0 gm/lit and 1.5 gms/lit. respectively are sufficient. (Vide Graph No.C:1 and 2).
6. The % of maximum extractability of Chromium (VI) is found to be 97.1% with the powders leaves of *Achyranthes aspera* at pH: 2 and after an equilibration period of 4 hrs. with sorbent concentration of 2.0 gms/lit while with its ashes, the % of extraction has been increased to 100 % at pH:2 and after an equilibration period of 1.5 hrs with the sorbent concentration of 1.5 gm/lit. At pH:2 and at equilibration period of 2.0 hrs, % of extraction is found to be 96.8% with leaves powder of *Mentha* at sorbent concentration of 2.5 gm/lit while 98.8% with their ashes at pH:2 and at equilibration of 1.5 hrs and the sorbent concentration of 2 gm/lit. At pH: 2 and at optimum equilibration time and sorbent concentrations, the % of maximum extractability is found to be 96.0%, 95.0%, 93.0% and 92.0% for the sorbents: leaves powders of *Embolica officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum* respectively and with their ashes the % of maximum extractability is found to be 97.0%, 97.8%, 95.0% and 94.5% respectively (vide Graph No. A:1-12)
7. Interfering Ions: The extractability 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 and Nickel

ions, has been studied. The results are presented in Table No. 1.

- Cations chosen for study have been found to *have less effect* on the extractability of Chromate with the sorbents of the present work at the optimum conditions of time of equilibration, pH and sorbent concentration; the % of extractions of Chromate is found to be between 88.0% to 99.2%.
- Anions: SO_4^{2-} is found to be interfering to some extent with the powder of Mentha Leaves and Emblica officinalis leaves and with ashes of the latter (vide S. Nos. 2, 3 and 9) and with the rest of the sorbents, the interference is marginal. Ten fold excess of NO_3^- is found to decrease the % of extractability of Chromate *only* in the case of powder of Mentha leaves and Ashes of Hibiscus roja sinensis and Ocimum sanctum leaves and not with the other sorbents. (vide S. No. 2, 11 and 12 in the 5th Column of Table No.1). Chloride shows less interference except in the case of powder of Emblica officinalis and Hibiscus roja sinensis leaves and ashes of the former (vide S.No.3,5 & 9 in the column 6 of Table No. 1). Phosphate is found to interfere the extraction with respect to the sorbents: powders of Azadirachta india leaves and its ashes and also with the ashes of Hibiscus roja sinensis and Ocimum sanctum leaves (vide S. No. 4, 10-12 of Table No. 1). Fluoride has been found to be interfering in the case of all powders of leaves except Mentha leaves powder but with ashes as sorbents, the interference is found only in the case of Azadirachta indica (vide S.No. 1,3-6 and 10). *Though the said ions show some interference in some sorbents of study, % of extraction of Chromates has never come below 60.0%. This quite interesting observation.*



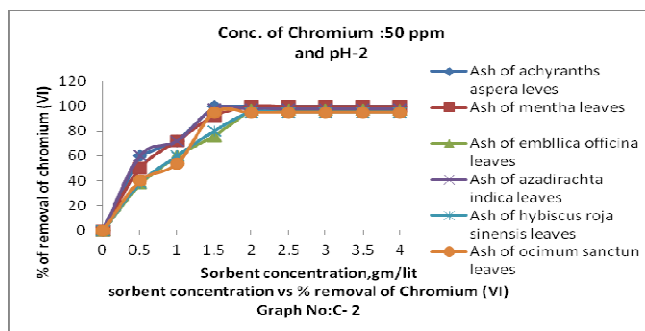
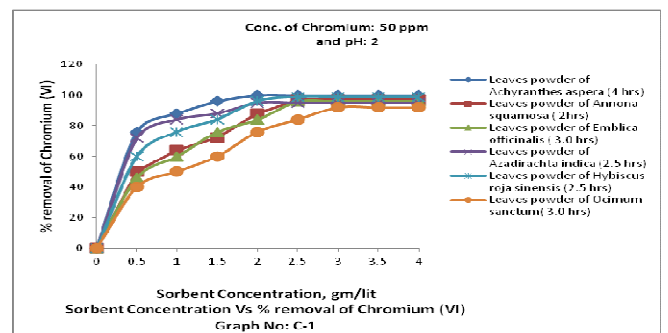
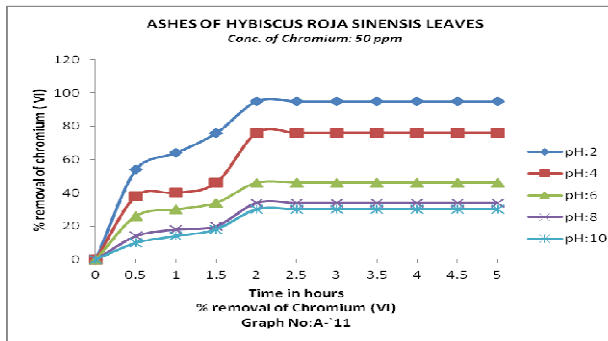
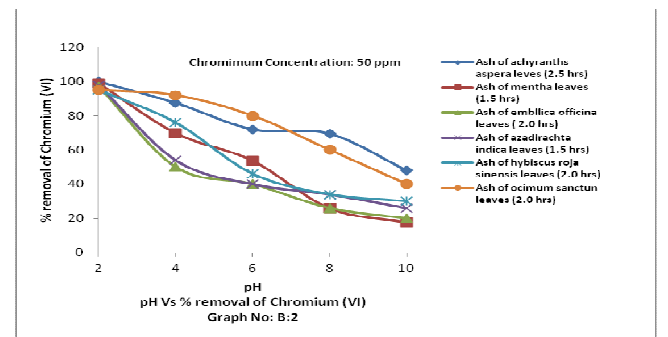
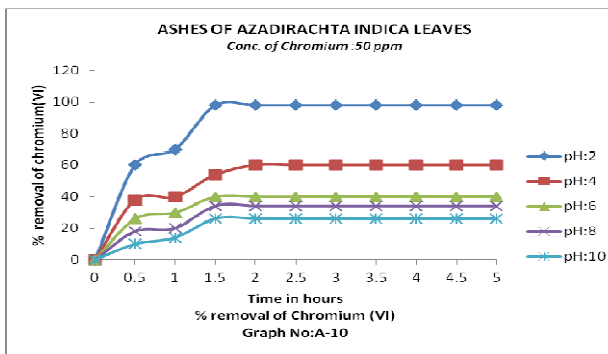
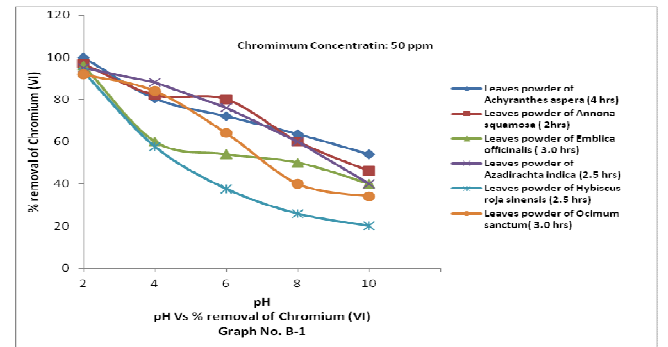
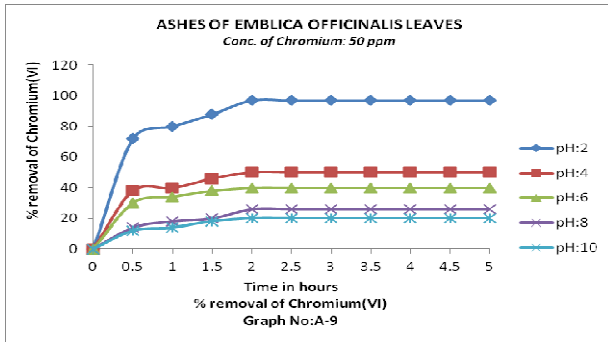
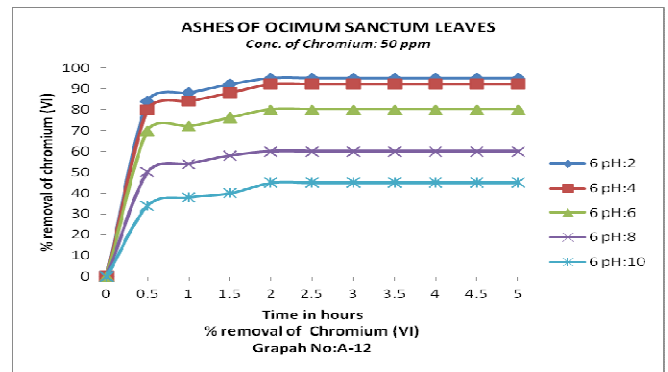
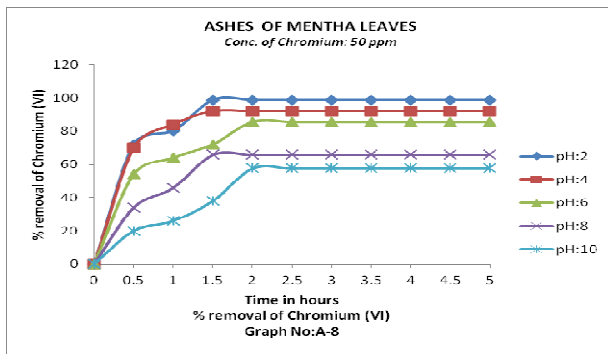


Table No 1. Effect of interfering Ions on the Extractability of Chromates with different Bio-sorbents

S.No	Adsorbent and its concentration	Maximum Extractability at optimum conditions	Extractability of Chromate in presence Tenfold excess of (500ppm) interfering ions at optimum conditions: Conc. of Chromium(VI): 50 ppm										
			SO ₄ ²⁻	NO ₃ ²⁻	Cl ⁻	PO ₄ ³⁻	F ⁻	CO ₃ ²⁻	Ca ²⁺	Mg ²⁺	Cu ²⁺	Zn ²⁺	NI ²⁺
1	Powder of <i>Achyranthes aspera</i> leaves: 2.0 gms/lit	97.1%; pH:2, 4.0hrs	99.2 %	98.9%	84.0%	99.6%	70.0%	99.0%	96.2%	98.2%	97.1%	99.2%	96.2%
2	Powder of <i>Mentha</i> leaves 2.5gms/lit	96.8% pH:2, 2.0 hrs	78.6%	79.5%	80.0%	80.6%	84.2%	88.0%	96.7%	96.7%	95.6%	95.2%	93.1
3	Powder of <i>Emblica officinalis</i> leaves; 3.0 gms/lit	96.0% pH:2, 3.0hrs	64.0%	95.0%	64.0%	95.0%	60.1%	94.1%	95.0%	93.0%	96.0%	92.5%	96.0%
4	Powder of <i>Azadirachta indica</i> leaves; 2.0 gms/lit	95.0% pH:2, 2.0 hrs	94.0%	94.0%	94.0%	64.0%	60.1%	60.1%	92.0%	92.4%	94.1%	93.1%	93.0%
5	Powder of <i>Hybiscus roja sinensis</i> leaves 2.5 gms/lit	93.0% pH:2, 2.5 hrs	92.0%	92.0%	70.1%	93.0%	60.0%	92.7%	93.0%	92.0%	92.0%	88.0%	91.0%
6	Powder of <i>Ocimum sanctum</i> leaves; 2.0 gms/lit	92.0% pH:2, 3.0 hrs	91.0%	90.0%	90.0%	92.0%	64.0%	92.0%	91.0%	90.0%	89.0%	91.0%	92.0%
7	Ashes of <i>Achyranthes aspera</i> leaves: 1.5 gms/lit	99.8%; pH:2, 2.5 hrs	99.2%	99.6%	88.0%	99.0%	80.0%	97.0%	96.0%	98.9%	96.0%	97.4%	96.0%
8	Ashes of <i>Mentha</i> leaves 2.0 gms/lit	98.8% pH:2, 1.5 hrs	80.0%	84.0%	92.0%	96.0%	84.0%	96.0%	96.0%	97.4%	95.0%	92.0%	94.0%
9	Ashes of <i>Emblica officinalis</i> leaves 2.0 gms/lit	97.0% pH:2, 2.0hrs	72.0%	96.0%	76.0%	96.0%	80.0%	94.0%	92.0%	96.0%	95.0%	94.0%	92.0%
10	Ashes of <i>Azadirachta indica</i> leaves 1.5 gms/lit	97.8%; pH:2; 1.5 hrs	94.0%	92.0%	92.0%	60.0%	72.0%	96.0%	97.4%	95.0%	92.0%	93.0%	94.0%
11	Ashes of <i>Hybiscus roja sinensis</i> leaves ; 2.0 gms/lit	95.0% pH:2, 2.0 hrs	95.0%	72.0%	94.0%	72.0%	88.0%	94.8%	93.0%	94.0%	92.0%	90.0%	93.0%
12	Ashes of <i>Ocimum sanctum</i> leaves; 2.0 gms/lit	94.5% pH:2, 2.0 hrs	94.0%	76.0%	93.1%	60.2%	84.0%	94.1%	92.0%	94.0%	91.0%	94.2%	90.1%

Table No 2. Extractability of Chromates in Different Industry and Natural Samples

Bio-Sorbent	% of Extractability of Chromates in diverse Samples (actual conc. of Chromate is shown in parenthesis)								
	Tannery Industry effluents			Chrome plating Industry effluents			Natural Lake Samples		
	S-1 (12.5 ppm)	S-2 (21.5 ppm)	S-3 (14.5 ppm)	S-4 (21.5 ppm)	S-5 (24.5 ppm)	S-6 (15.8 ppm)	S-7 (15 ppm)	S-8 (20 ppm)	S-9 (25 ppm)
Leaves powder of <i>Achyranthes aspera</i> :at pH:2; Equilibration time: 6 hrs and sorbent concentration: 1.5 gm/lit	84.3%	89.8%	85.5%	83.5%	88.2%	90.2%	87.8%	89.4%	86.5%
Leaves powder <i>Mentha</i> : at pH:2; Equilibration time: 6 hrs and sorbent concentration: 2.0 gm/lit	80.4%	79.8%	80.5%	81.5%	82.2%	82.5%	81.8%	83.4%	84.5%
Leaves powder of <i>Emblica officinalis</i> :at pH:2; Equilibration time: 6 hrs and sorbent concentration: 4.0 gms/lit	69.4%	74..8%	75.5%	74.5%	78.4%	80.2%	83.8%	84.4%	85.5%
Leaves powder of <i>Azadirachta indica</i> :at pH:2; Equilibration time: 6 hrs and sorbent concentration: 4.0 gm/lit	74.3%	69.8%	65.5%	63.5%	68.2%	64.2%	67.8%	68.4%	66.5%
Leaves powder of <i>Hybiscus roja sinensis</i> :at pH:2; Equilibration time: 5 hrs and sorbent concentration: 1.0 gm/lit	74.3%	72.8%	75.5%	73.5%	74.2%	79.2%	78.8%	79.4%	76.5%
Leaves powder of <i>Ocimum sanctum</i> at pH:2; Equilibration time: 5 hrs and sorbent concentration: 1.0 gm/lit	90.4%	88.1%	91.4%	88.6%	89.3%	91.6%	89.8%	87.3%	85.5%
Ashes of Leaves of <i>Achyranthes aspera</i> :at pH:2; Equilibration time: 5 hrs and sorbent concentration: 2.0 gms/lit	84.5%	89.4%	94..8%	92.5%	88.5%	91.4%	93.2%	94.8%	93.4%
Ashes of Leaves powder <i>Mentha</i> :at pH:2; Equilibration time: 5 hrs and sorbent concentration: 2.0 gm/lit	92.4%	94..8%	89.6%	94.4%	88.7%	90.2%	94.8%	96.4%	95.5%
Ashes of Leaves powder : <i>Emblica officinalis</i> at pH:2; Equilibration time: 5 hrs and sorbent concentration: 2.0 gm/lit	73.3%	79.8%	80.8%	90.5%	93.2%	94.2%	96.8%	90.4%	96.5%
Ashes of Leaves powder <i>Azadirachta indica</i> :at pH:2; Equilibration time: 5 hrs and sorbent concentration: 2.0 gm/lit	73.3%	89.8%	87.5%	88.5%	84.6%	89.2%	88.8%	89.4%	76.5%
Ashes of Leaves powder of <i>Hybiscus roja sinensis</i> :at pH:2; Equilibration time: 5 hrs and sorbent concentration: 2.0 gm/lit	78.3%	86.8%	84.8%	91.5%	93.6%	92.2%	89.8%	91.4%	92.5%
Ashes of Leaves powder of <i>Ocimum sanctu</i> :at pH:2; Equilibration time: 5 hrs and sorbent concentration: 2.0 gm/lit	77.3%	88.8%	87.4%	92.5%	91.6%	90.2%	91.8%	89.8%	87.5%

APPLICATIONS

The Applicability of the methodology developed in this work has been tested with respects to diverse samples collected from the sewages/effluents of Tannery and Chrome plating industries and natural lakes. The results have been presented in the Table No: 2.

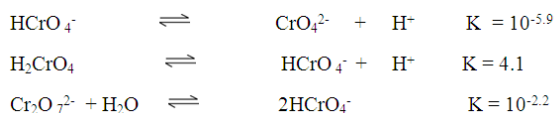
It is found that the sorbents developed in this work are successful in removing Chromates at optimum conditions of pH, equilibration time and sorbent dosage. % removal of Chromates is found to be: 83.5 to 90.2% with leaves powder of *Achyranthes aspera* and 84.5% to 94.8% with their ashes.; 79.8% - 84.5% with leaves powder of *Mentha* and 89.6% to 96.4% with their ashes; 69.4% to 85.5% with the leaves powder of *Emblica officinalis* and 73.3% to 96.8% with their ashes; 63.5% to 74.3% with the leaves powder of *Azadirachta indica* and 73.3% to 89.8% with their ashes; 72.8% to 79.4% with the leaves powder of *Hybiscus roja sinensis* and 78.3% to 93.6% with their ashes; and 85.5% to 91.6% with the leaves powder of *Ocimum sanctum* and 77.3% to 92.5% with their ashes.

DISCUSSIONS

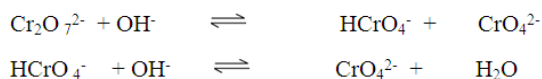
To propose sound theoretical grounds for the each observation made is rather complicated and it needs further deep thorough study with regard to surface characteristics of the sorbents, and their sorption nature with respect to the adsorbates (Chromate) using more sophisticated instruments and methodologies and it is beyond the endeavor of this work. However, the behaviors may generally be understood as follows:

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 .

1. The equilibria are the following:

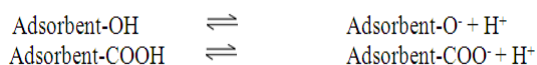


In addition there are the base hydrolysis equilibria:



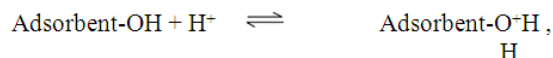
Thus the nature of the species is the pH dependent and further Chromate salts of most of the metallic ions are insoluble in water

2. The lingo celluloses' materials have -OH/COOH groups and their dissociation is pH dependent. At high pH values, these groups dissociates as:



and imparts weak cation exchange ability and at low pH

values, the dissociation is less favored and protination may also occur:



resulting weak anion-exchange ability. This is reflected in sorption of Chromate. Chromate being an anion in the pH range: 2-6, is adsorbed by these materials at low pHs and thus results in higher % of removal. As pH increases, the deprotonation occurs and hence the affinity of the adsorbent towards the Chromate decreases and thus resulting in low % removal of Chromate ions.

- The decrease in the rate of sorption with the progress in the equilibration time may be due to the more availability of sorption sites initially and are progressively used up with time due to the formation of adsorbate: Chromate, film on the sites of the sorbent and thus resulting in decrease in sorption ability of the adsorbents.
- Further, some of the divalent or trivalent metal ions form salts with of Chromate which are sparingly or insoluble in water. Naturally occurring adsorbents chosen for study, contain some impurities of metal ions like Ca, Cu, Zn, Fe, Mn, Ba, Pb. Hence the Chromate forms insoluble or sparingly soluble salts with these cation impurities present in the powders of leaves and barks or in their ashes. Most of 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 Chromium. This is more so in the case of ashes, which are oxides of some metal ions.
- Ashes are the oxides of some heavy metals containing large amounts of silica. The ashes, contains '-OH' groups and '-O-'. 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 lingo cellulose materials. In fact, the transition pH for silica from anion exchanging nature to cation exchanging nature is 3 [38-40] and this supports the proposed logic for the observed behavior. Further, the formation of sparingly soluble salts with the metallic ions present in the ashes may also contribute to the extraction 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, Chromate, on the sites of adsorbent and thus resulting in decrease in capability of the adsorbent.

CONCUSSIONS

- Powders of leaves of *Achyranthes aspera*, *Mentha*, *Emblica officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum* have been found to have strong affinity towards Chromate at low pH values.
- % of removal of Chromate is pH sensitive and also depends on sorption concentration and time of equilibration

3. The minimum dosage and equilibration time needed for the maximum removal of Chromate is less for the ashes of leaves than with the raw leaves powders.
4. Ten fold excess of common cation ions present in natural waters, viz., Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} and Ni^{2+} have less affected the % of extraction of Chromate at optimum conditions of pH, equilibration time and sorbent concentration. But some anions when present in tenfold excess showed some interference with some sorbents as shown in the Table No: 2. Sulphates, Nitrate, Cl^- , Phosphate and F^- have shown this kind of nature.
5. We claim 97.1%, 96.8%, 96.0%, 95.0%, 93.0% and 92.0% of removal of Chromate from synthetic waters with the leaves powders of *Achyranthes aspera*, *Mentha*, *Emblica officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum* respectively at pH:2, and at optimum of equilibration time and optimum sorbent concentrations. The % of removal is enhanced to 100%, 98.8%, 97.0%, 97.8%, 95.0% and 94.5% with the ashes of *Achyranthes aspera*, *Mentha*, *Emblica officinalis*, *Azadirachta indica*, *Hybiscus roja sinensis* and *Ocimum sanctum* at pH:2, and at low equilibration times and sorbent concentrations.
6. The suitability of the developed sorbents are tested with respect to diverse waste water samples collected in nine different places. Most of the sorbents developed in this work have been found to be successful in removing the Chromate from industrial effluents and natural lake samples as detailed in Table No:2

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