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STEMS AND THEIR ASHES OF SOME HERBAL PLANTS AS ADSORBENTS IN THE REMOVAL OF CHROMIUM (VI) FROM WASTE WATERS

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ABSTRACT: A thorough investigation is made to explore the surface sorption abilities of powders of stems and their ashes of some herbal plants in controlling the Chromium (VI) pollution in waste waters. It is found that the powders of stems and their ashes of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis, Ocimum sanctum and Psidium guajava have strong affinity towards Chromate at low pH values. % of removal of Chromate is found to be pH sensitive and also depends on sorption concentration and time of equilibration. The conditions for the maximum extraction of Chromate at minimum dosage of sorbent and equilibration time have been optimized. More than 90.0% of removal of Chromate is found. Sorbent concentrations and time needed for the maximum removal of Chromate is less for the ashes of stems than with the raw stem powders. The presence of ten fold excesses of Cations : Ca^{2+}, Mg^{2+}, Cu^{2}, Zn^{2+} and Ni^{2+} and anions like NO_3^- ,Chloride, Fluoride and Carbonate have ***marginally*** effected the % removal of Chromium (VI) while Sulphate and Phosphate showed some interference with some sorbents but even with them, the % of extractability never comes down to 71.0%. 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.

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

INDTRODUCTION

Chromium compounds are being intensively used in modern industries such as textile, dyeing, leather tanning, electroplating and metal finishing and this results in the discharge of good quantities of Chromium compounds through effluents into the environment. The accumulation of Chromium (VI) through waste discharges into the natural water bodies causes serious problems due to its possible entry into the food chain and results in bio-amplification [1-3]. The hexavalent Chromium, considered being the most toxic, causes skin irritation which results in ulcer formation, liver damage, pulmonary congestion and oedema and it is a group “A” human carcinogen because of its mutagenic and carcinogenic properties[1-6]. Its permissible limit is: 0.05-1 ppm in waste and disposable waters. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 µg/ml and US. EPA primary drinking water standard is 0.1 ppm of total Chromium [6].

Wide ranges of methods are available for the removal of hexavalent Chromium from wastewaters and some of which are well-established methods that have been in practice for decades such as precipitation, co-precipitation, concentration and Chemical reduction [5, 7-9]. Most of these methods produce solid residues containing toxic compounds whose final disposal is generally by land filling and this involves high costs and further, there exists a great danger of groundwater contamination. From the environmental point of view, these methods do not solve the problem and it transfers it from one phase to another phase. Further, these methodologies are un-satisfactory when the concentration of Chromium is less.

Growing research interest is seen in recent years in developing methods for recovery and reuse of costly pollutants and more emphasis is being envisaged on the applicability of the methods for minute concentration of Chromium. Nanofiltration [10], bioaccumulation [11], ion exchange [12] ,adsorption on silica composites [13, 14], activated carbons [15], fly Ash [16], modified zeolites [17,18] and bone charcoal [19] have been explored for the removal of Chromium from waste waters. Ashalatha Singh reviewed the various methods available in literature in removing Chromium from waste waters using microbes [20]. A number of patents also are existing in this regard [21]. These techniques, apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements and generation of toxic sludges or other waste products that require disposal. Hence efficient and environmentally friendly methods are thus needed.

In this context, increasing focus is being envisaged by researches in recent years in developing methodologies in controlling Chromium pollution in waste water using bio-products , agricultural waste or masses by evoking their surface sorption potentialities[9, 22-31].

In the present work, the sorption characteristics of powders of stems and their ashes of some herbal plants have been studied for the removal of Chromium (VI) from polluted waters with respect to various physicochemical parameters such as pH, time of equilibration and sorbent concentration and we tried to develop simple methodologies in controlling the Chromium (VI) pollution in waste waters ***by optimizing the extraction conditions.***

METIRIALS AND METHODS

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.

A: Adsorbents:

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

Achyranthes aspera

Mentha

Emblica officinalis

Hibiscus rosa-sinensis

Osmium sanctum

Psidium guajava

Achyranthes aspera is herbal plant belong to Amaranthaceae family and is known to have medicinal values and it grown in tropical conditions. Mentha is an herbal plant belongs to Lamiaceae family and is well grown in moist conditions and it possesses medicinal values. Emblica officinalis is one of the most celebrated herbs in the Indian traditional medicine system and it belongs to Euphorbiaceae family and grows well in India. Hsibisuc rosa-sinensis is an ever green flowering shrub belongs to Malvaceae family and is grown throughout tropics and subtropics. Ocimum sanctum is an aromatic plant in the family of Lamiaceae. It is known in South Asia as a medicinal plant and has religious sanctity among Hindus. Psidium guajava is an ever green shrub or small tree widely cultivated in tropical and subtropical regions around the world and it belongs to Myrtaceae family.

The stems of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis , Ocimum sanctum and Psidium 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 activated at 105ºC in a oven and then employed in this study. Further, these stems were burnt to ashes and these ashes were also used in this work.

B: Adsorption experiment:

Batch system of extraction procedure was adopted [4, 5, 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 [32]

Estimation of Chromium (VI): An aliquot amount of Chromate sample was taken in a 50 ml 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 measured 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 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.

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 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 ***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 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 concentrations 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 No. 2.

RESULTS AND DISCUSSION

1. Of the various sorbets tried, the stems and their ashes of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis, Ocimum sanctum and Psidium guajava have been found to have affinity towards Chromates. The sorption characteristics of these adsorbents have been studied with respect to various physicochemical 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:

2. 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).
3. 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 stem powders of Achyranthes aspera, % of extractability, is found to be 38.0% at pH:10; 40.0% at pH:8; 46.0% at pH:6; 64.0% at pH:4 and 98.0% at pH: 2. In the case of ashes of Achyranthes aspera, the extraction of Chromium (VI) is found to be 34.0% at pH:10, 38.0% at pH:8 , 40.0% at pH:6, 60.0% at pH:4 and 99.9% at pH:2. The same trend is found in other sorbents also.
4. pH: % of extraction is found to be pH sensitive. As pH decreases, % of extraction is found to be increasing (Vide Graph: B: 1 and 2). As for example, with the stem powders of Mentha, % of extractability is found to be 26.0 % at pH:10; 38.0% at pH:8; 40.0% at pH:6; 54.0% at pH:4 and 94.0% at pH: 2 while with the ashes of stems of Mentha, % of extractability is found to be: 20.0% at pH:10, 34.2% at pH:8, 38.0% at pH:6, 70.0% at pH:4 and 98.8% at pH:2.

Similar trend is found in the case of other stem powders. At pH:2,4,6,8 and 10, the extractability of Chromium(VI) is found respectively to be: 95.8 %, 64.0%, 46.0%, 40.0% and 38.0% in the case of stem powders of Emblica officinalis after 3.5 hrs of equilibration time; 96.8%, 76.0%, 40.0%, 30.0% and 20.0 % in the case of powder of leaves of Hybiscus roja sinensis after 2.5 hrs of equilibration; 97.0%, 40.0%, 34.0%, 26.0% and 20.0% in case of powder of stems of Ocimum sanctum after 2.5 hrs of equilibration; 92.9%,40.0%,34.0%, 26.0% and 18.0% in case of powder of stems of Psidium guajava after 2.0 hrs of equilibration time.

In the case of ashes of stems of Emblica officinalis, 97.3%, 64.0%,54.0%, 40.0% and 38.0% have been found at pH: 2,4, 6,8 and 10 respectively at an equilibration period of 2.5 hrs; 98.0%,80.0%,46.0%,26.0%and 20.0% at equilibration time of 2hrs in the case of ashes of stems of Hybiscus roja sinensis ; 99.0%, 64.0%, 38.0%,26.0% and 20.0% at equilibration time of 2 hrs with ashes of stems of Ocimum sanctum; 99.5%, 64.0%,60.0%, 54.0% and 40.0% at equilibration time of 1.5 hrs with ashes of stems of Psidium guajava.

5 The maximum % of extractability is found to be marginally more with ashes of stems than with raw powders of stems.

6 In most of the sorbents, time of equilibration needed for maximum extractability of Chromate is found to be less for ashes than with the raw powder of stems. With stems powders of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis, Ocimum sanctum and Psidium guajava,, the equilibration time needed for maximum extraction is found to be 3.5 hrs, 3.0 hrs, 3.5 hrs, 2.5 hrs, 2.5 hrs and 2.0 hrs respectively at optimum pH: 2 while with their ashes, the optimum equilibration times are found to be 2.0 hrs, 2.5 hrs, 2.5 hrs, 2.0 hrs, 2.0 hrs and 1.5 hrs. respectively (vide Graph Nos. A:1-12).

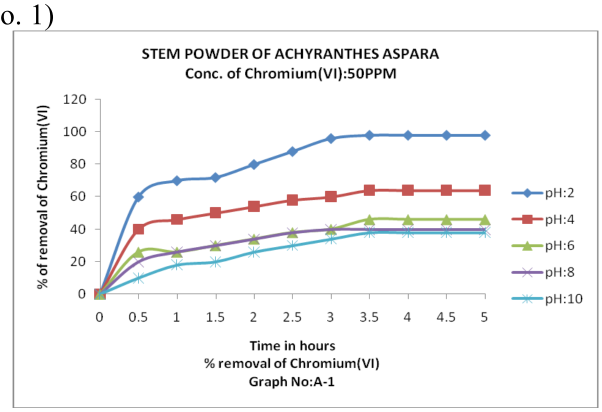
7 Sorbent Concentration: The sorbent dosage needed for maximum extraction of Chromate is found to be less in the case of stem powders than with their ashes. Sorbent concentration for maximum extraction at optimum conditions of pH and equilibration time is found to be 1.5 gram/lit for the stem powders of Achyranthes aspera while with its ashes optimum sorption concentration has been reduced to 1.0 gms/lit. Similarly, with the stem powders of Mentha, optimum sorbent concentration is 1.5 gm/lit but with their ashes, 1.0 gm/lit is sufficient. In the case of stem powders of Emblica officinalis, Hybiscus roja sinensis and Ocimum sanctum, the sorbent concentration needed is found to be 2.0 gms/lit while with their ashes, 1.5 gms/lit. is sufficient. With stem powders of Psidium guaja, sorption concentration needed is found to be 1.5 gm/lit while with their ashes the sorption concentration needed is reduced to 1.0 gm/lit.

8 The % of maximum extractability of Chromium (VI) at optimum conditions of pH and equilibration time are found to be 98.0%,94.0%, 95.8%, 96.8%, 97.0% and 92.9% in the case of stem powders of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis, Ocimum sanctum and Psidium guajava respectively (vide Graph Nos.A:1-6).

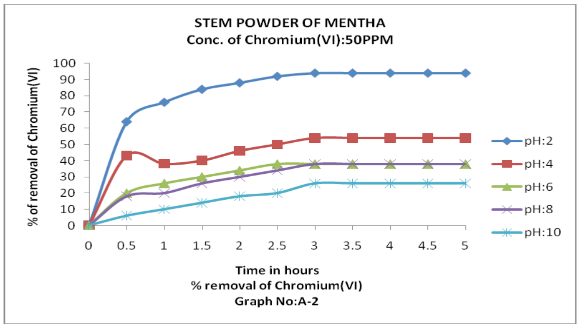
9 With ashes of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis, Ocimum sanctum and Psidium guajava , % of maximum extractability is found to be 99.9%, 98.8%,97.3%, 98.0%, 99.0% and 99.5% respectively at optimum conditions of pH: 2 and equilibration times of 2.0 hrs, 2.5 hrs, 2.5 hrs, 2.0 hrs,2.0 hrs and 1.5hrs respectively (vide Graph Nos .A: 7-12).

10 Interfering Ions: The extractability of Chromate 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 and Nickel ions, has been studied. The results are presented in Table No. 1.

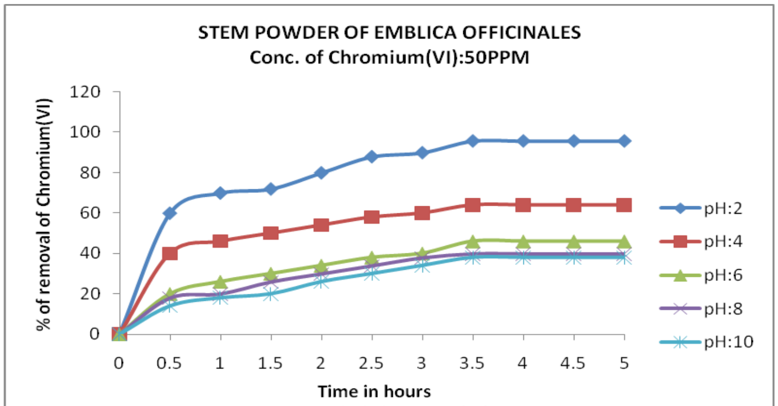
- Cations
  - Envisaged marginal effect on the % extractability of Chromate with the sorbents of the present work at the optimum conditions of time of equilibration, pH and sorbent concentration. % of extraction of Chromate is found to be between 90.9% to 97.5% with stem powders of Achyranthes aspera and 91.6% to 99.0% with its ashes; 89.2% to 92.7% with stem powders of Mentha and 90.4% to 97.4% with its ashes; 91.2% to 95.0% with stem powders of Emblica officinalis and 93.1% to 96.0% with its ashes; 90.7% to 95.0% with stem powders of Hybiscus roja sinensis and 89.6% to 95.1% with its ashes; 91.0% to 95.7% with stem powders of Ocimum sanctum and 92.0% to 98.3% with its ashes; and 86.2% to 91.2% with stem powders of Psidium guajava and 89.6% to 95.0% with its ashes.
- Anions:
  - SO_4^{2-} is found to be interfering to some extent with the stem powders of Achyranthes aspera and Hybiscus roja sinensis and ashes of stems of Mentha and Psidium guajava (vide S. No. 1,4,8 and 12 of Table Nos:1) and in the reset of the sorbents, the extractability of Chromates is seldom effected.
  - Ten fold excess of NO_3^- , Chloride, Fluoride and Carbonate are found to have marginal interference with the % of extractability of Chromate in all the sorbents of interest (vide 5th,6th, 8th and9th Column of Table No. 1).
  - Phosphate is found to be interfering with the extraction of Chromate with stem powders of Achyranthes aspera, Emblica officinalis, Hibiscus roja sinensis and Ocimum sanctum and in the ashes of stems of Achyranthes aspera and Hybiscus roja sinensis. (Table No.1: 7th Column). However, the extractability never comes down below 71.0%. In the remaining sorbents, the % of extractability is almost un-effected (Vide 6th column of Table No. 1)



% removal of Chromium(VI)
Graph No:A-1

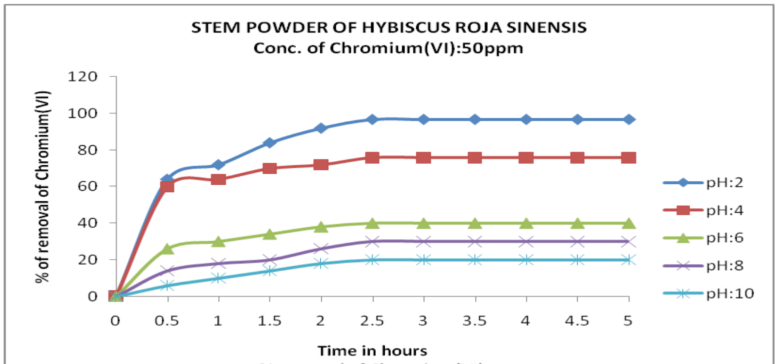


% removal of Chromium(VI)
Graph No:A-2



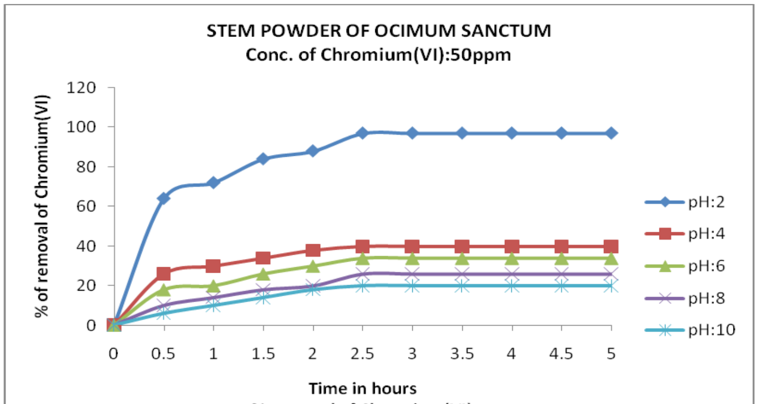
% removal of Chromium(VI)

Graph No:A-3



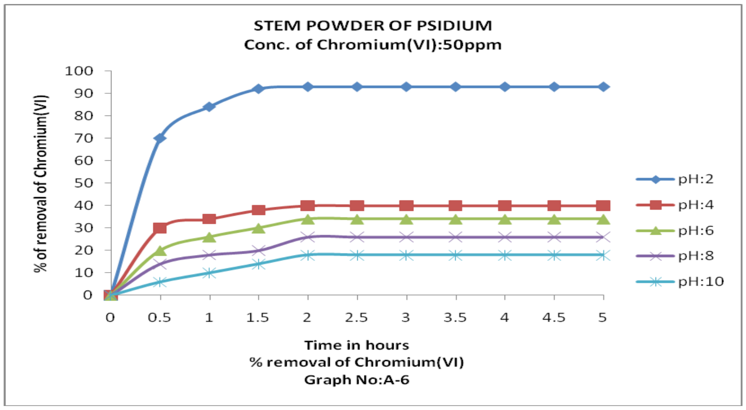
% removal of Chromium(VI)

GraphNo:A-4

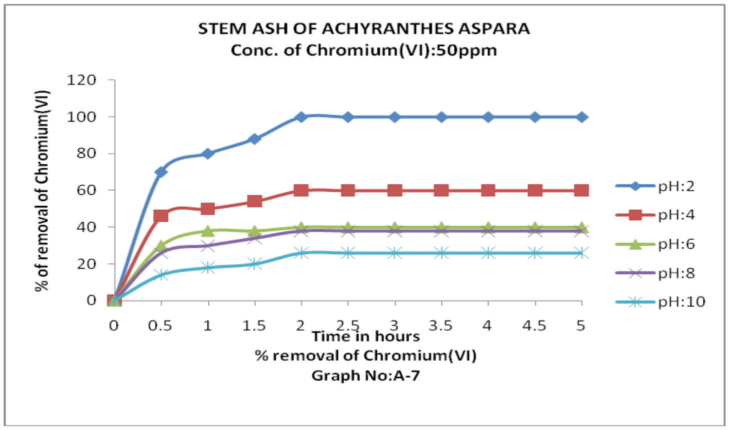


% removal of Chromium(VI)

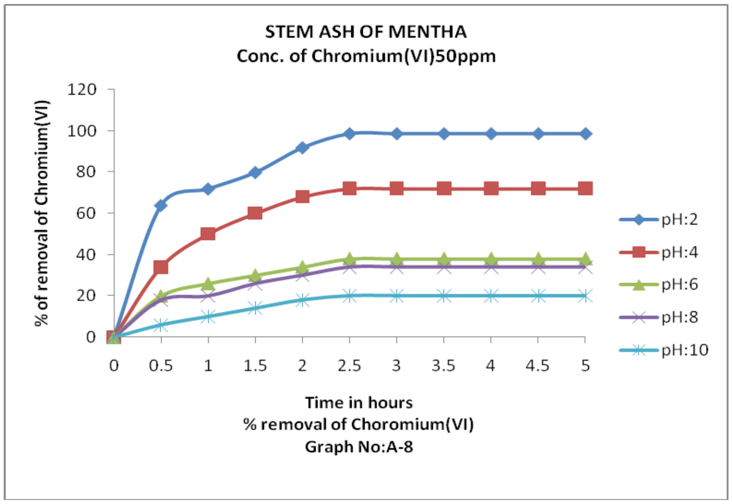
Graph No:A-5


STEM POWDER OF PSIDIUM
Conc. of Chromium(VI):50ppm

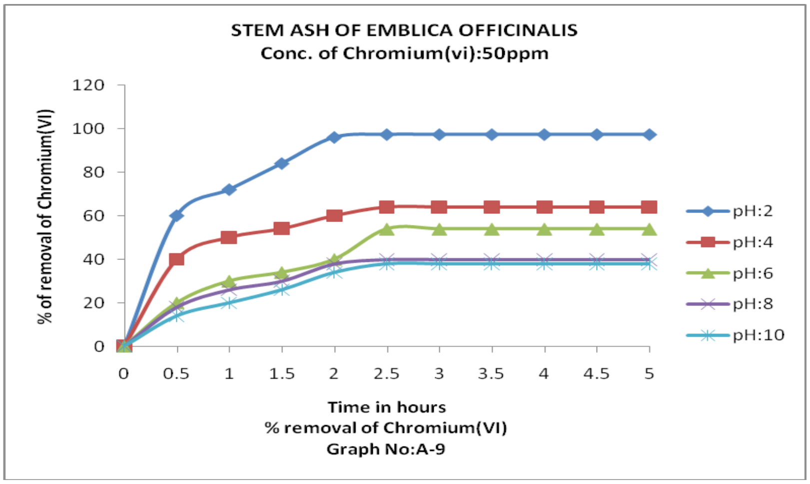
Time in hours
% removal of Chromium(VI)
Graph No:A-6

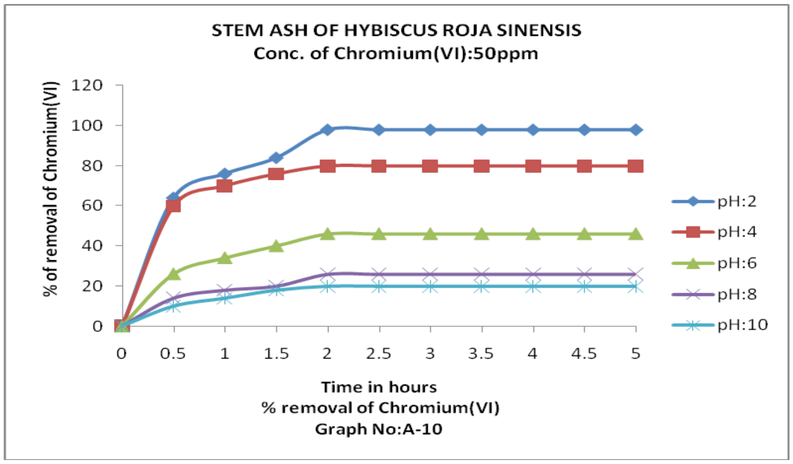

STEM ASH OF ACHYRANTHES ASPARA
Conc. of Chromium(VI):50ppm

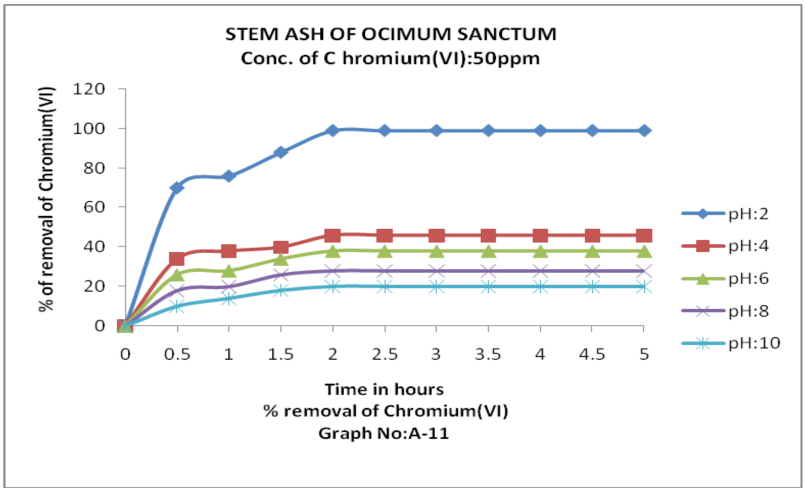
Time in hours
% removal of Chromium(VI)
Graph No:A-7

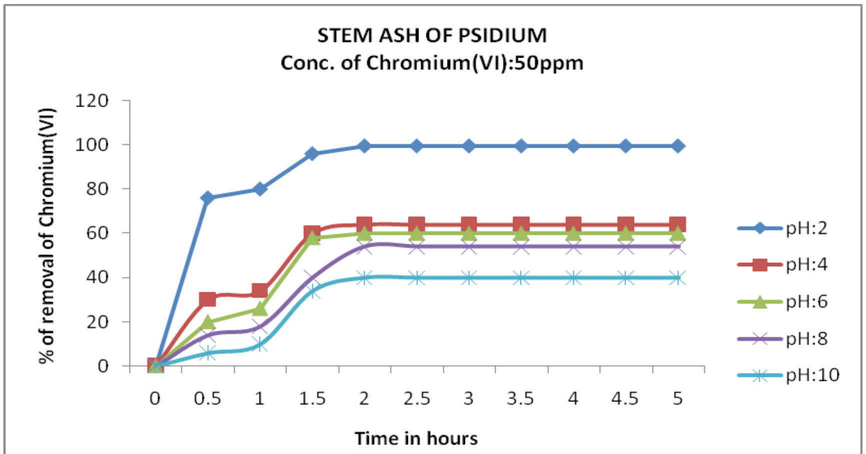

STEM ASH OF MENTHA
Conc. of Chromium(VI)50ppm

Time in hours
% removal of Choromium(VI)
Graph No:A-8

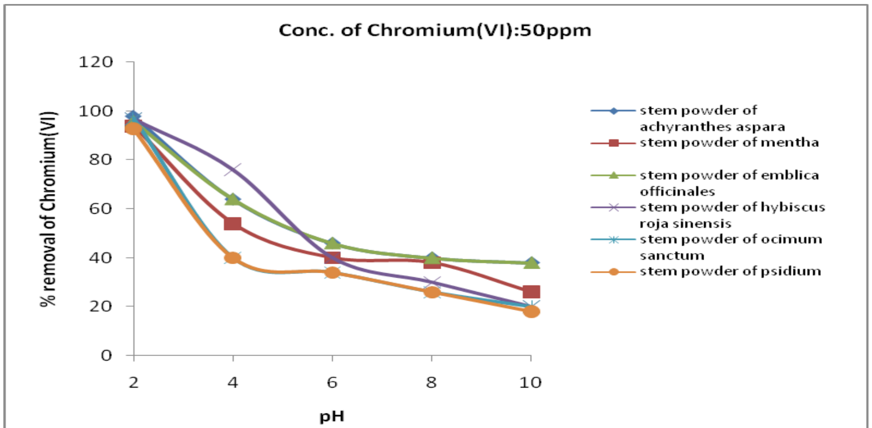

STEM ASH OF EMBLICA OFFICINALIS
Conc. of Chromium(vi):50ppm
% of removal of Chromium(VI)
120
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
pH:2
pH:4
pH:6
pH:8
pH:10
Time in hours
% removal of Chromium(VI)
Graph No:A-9


STEM ASH OF HYBISCUS ROJA SINENSIS
Conc. of Chromium(VI):50ppm
% of removal of Chromium(VI)
120
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
pH:2
pH:4
pH:6
pH:8
pH:10
Time in hours
% removal of Chromium(VI)
Graph No:A-10

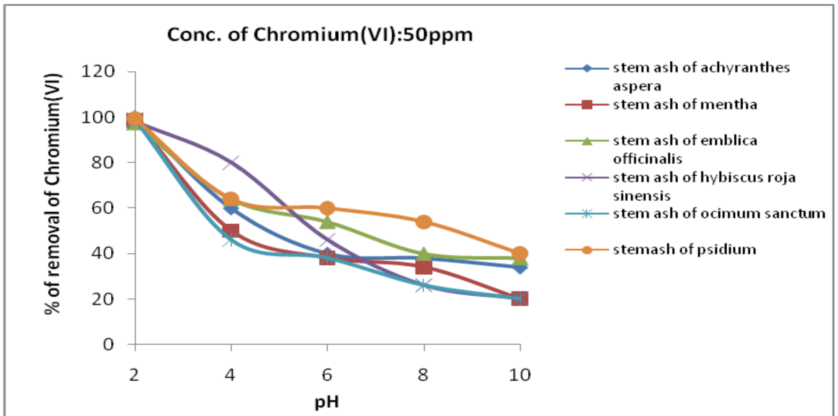

STEM ASH OF OCIMUM SANCTUM
Conc. of C hromium(VI):50ppm
% of removal of Chromium(VI)
120
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
pH:2
pH:4
pH:6
pH:8
pH:10
Time in hours
% removal of Chromium(VI)
Graph No:A-11



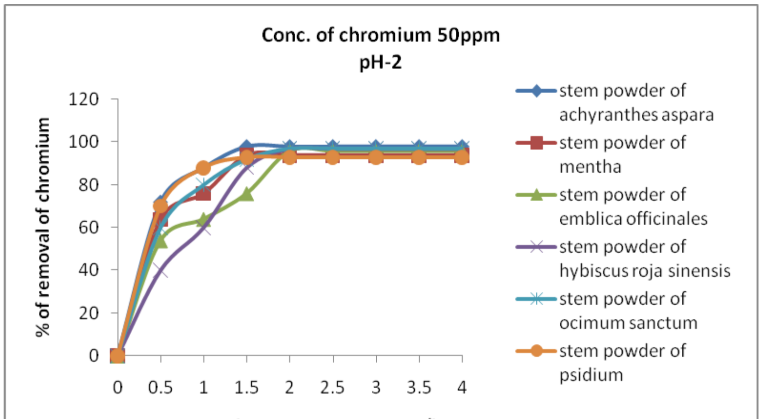
% removal of Chromium(VI)
graph No:A-12



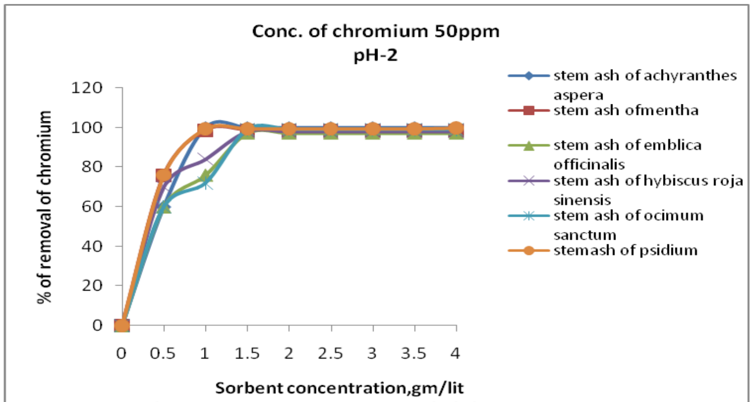
pH vs % removal mof Chromium(VI)
Graph No:B-1



pH vs % removal of Chromium(VI)
Graph No:B-2



sorbent concentration vs % removal of chromium
Graph No:C-1



sorbent concentration vs % removal of chromium
Graph No:C-2

Applications

The Applicability of the methodologies developed in this work have been tested with respects to the real samples of diverse nature, collected from the sewages/effluents of Tannery and Chrome plating industries and also in natural 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 successful in removing Chromates in all the samples studied at optimum conditions of pH, equilibration time and sorbent dosage. % removal of Chromates is found to be: 88.9% to 97.8% with stem powders of Achyranthes aspera ; 80.2% to 93.9% with stem powders of Mentha; 81.9% to 94.5% with stem powders of Emblica officinalis; 71.3% to 93.8% with stem powders of Hybiscus roja sinensis; 70.8% to 95.8% with stem powders of Ocimum sanctum; 83.2% to 94.4% with stem powders of Psidium guajava. (vide Table No.2)

The % of extractability of Chromium in nine different samples ranges from 88.5% to 98.4% with the ashes of stems of Achyranthes aspera; 88.4% to 96.1% with ashes of Mentha stem powders; 75.9% to 95.4%with the ashes of Emblica officinalis; 77.5% to 90.5% with the ashes of Hybiscus roja sinensis; 76.9% to 96.3% with the ashes of Ocimum sanctum; and 78.1% to 93.4% with the ashes of Psidium guajav (vide Table No.2)

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 Ten fold 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	Stem powder of Achyranthes aspera: 1.5 gms/lit	98.0%; pH:2, 3.5hrs	76.3 %	92.8%	90.1%	79.4%	93.2%	96.6%	94.2%	97.5%	90.9%	92.7%	93.8%
2	Stem powder of Mentha 1.5gms/lit	94.0% pH:2, 3.0 hrs	87.2%	90.9%	92.1%	94.0%	93.2%	91.5%	89.2%	90.6%	92.7%	92.0%	92.6%
3	Stem powder of Emblica officinalis; 2.0 gms/lit	95.8% pH:2, 3.5hrs	93.6%	90.5%	94.5%	82.6%	91.2%	93.1%	93.7%	92.0%	94.6%	91.2%	95.0%
4	Stem powder of Hybiscus roja sinensis;2.0 gms/lit	96..8% pH:2, 2.5hrs	74.6%	95.2%	93.2%	78.7%	87.2%	89.6%	94.2%	95.0%	93.51 %	90.7%	91.8%
5	Stem powder of Ocimum sanctum 2.0 gms/lit	97.0% pH:2, 2.5 hrs	96.4%	90.7%	95.1%	71.0%	89.4%	96.3%	95.7%	92.5%	91.0%	93.8%	94.0%
6	Stem Powder of Psidium;1.5 gms/lit	92.9% pH:2, 2.0 hrs	89.6%	87.4%	91.2%	88.0%	90.0%	91.5%	86.2%	90.6%	91.2%	89.4%	90.3%
7	Stem Ashes of Achyranthes asper: 1.0 gms/lit	99.9%; pH:2, 2.0 hrs	93.2%	96.0%	92.1%	76.2%	90.4%	97.4%	95.1%	96.2%	99.0%	91.6%	97.9%
8	Stem Ashes of Mentha 1.0 gms/lit	98.8% pH:2, 2.5 hrs	77.2%	97.1%	90.3%	92.6%	96.3%	98.1%	97.4%	96.9%	93.7%	91.9%	90.4%
9	Stem Ashes of Emblica officinalis leaves 1.5 gms/lit	97.3% pH:2, 2.5hrs	91.4%	90.0%	96.2%	94.5%	95.0%	92.6%	93.1%	96.0%	94.0%	96.0%	95.7%
10	Stem Ashes Hybiscus roja sinensis 1.5 gms/lit	98.0%; pH:2; 2.0 hrs	97.6%	91.0%	88.0%	84.1%	93.4%	95.8%	89.6%	92.6%	94.8%	95.1%	93.4%
11	Stem Ashes of Ocimum sanctum ;1.5 gms/lit	99.0% pH:2, 2.0 hrs	96.0%	94.2%	91.2%	89.3%	90.7%	95.0%	92.0%	98.3%	93.1%	92.7%	90.8%
12	StemAshes of Psidium; 1.0 gms/lit	99.5%, pH:2, 1.5hrs	71.4%	91.3%	94.2%	93.6%	96.0%	93.3%	95.0%	89.6%	92.0%	91.0%	93.6%

DISCUSSION

The available data is in adequate to propose sound theoretical explanations for each observation made as it needs surface studies of "adsorbent and adsorbate interactions" using more sophisticated instruments and methodologies and it is beyond the aims of this 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.
- Further, these natural substances have -OH/COOH groups and their dissociation is pH dependent and this imparts weak anion exchange ability at low pH values and weak cation exchange ability at high pH values as per the equilibrations:

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

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

At low pH values: $\text{Adsorbent-OH} + H^+ \rightleftharpoons \text{Adsorbent-O}^+H_2$

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

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 (21.5ppm)	S-5 (24.5 ppm)	S-6 (15.8ppm)	S-7 (15 ppm)	S-8 (20 ppm)	S-9 (25 ppm)
Stem powder of Achyranthes aspera :at pH:2; Equilibration time: 3.5 hrs and sorbent concentration: 1.5 gm/lit	97.8.%	95.4%	94.6%	92.7%	88.9%	91.2%	89.0%	93.5%	90.2%
Stem powder Mentha: at pH:2; Equilibration time: 3.0 hrs and sorbent concentration: 1.5 gm/lit	92.0.%	86.4%	90.7%	87.9%	80.2%	89.6%	91.3%	93.9%	83.6%
Stem powder of Emblica officinalis :at pH:2; Equilibration time: 3.5 hrs and sorbent concentration:2.0 gms/lit	82.1%	84.9%	92.6%	90.5%	89.4%	81.9%	83.8%	94.5%	91.6%
Stem powder of Hybiscus roja sinensis :at pH:2; Equilibration time: 2.5 hrs and sorbent concentration: 2.0 gm/lit	93.8%	74.7%	85.3%	73.8%	71.3%	82.3%	90.3%	92.4%	78.5%
Stem powder of Ocimum sanctum :at pH:2; Equilibration time: 2.5 hrs and sorbent concentration: 2.0 gm/lit	70.8%	72.8%	74.9%	73.8%	75.2%	80.0%	88.2%	90.3%	95.8%
Stem powder Psidium at pH:2; Equilibration time: 2.0hrs and sorbent concentration: 1.5 gm/lit	92.4%	89.3%	90.5%	86.7%	86.5%	94.4%	88.9%	87.3%	83.2%
Stem Ashes of Achyranthes aspera :at pH:2; Equilibration time: 2.0 hrs and sorbent concentration1.0 gms/lit	85.7%	88.5%	92.6%	94.7.%	89.3%	94.5%	96.2%	97.3%	98.4%
Stem Ashes of Mentha :at pH:2; Equilibration time: 2.5 hrs and sorbent concentration: 1.0 gm/lit	93.1%	92.2%	90.6%	95.3%	89.2%	91.8%	88.4%	94.5%	96.1%
Stem Ashes of: Emblica officinalis at pH:2; Equilibration time: 2.5 hrs and sorbent concentration: 1.5 gm/lit	75.9%	78.3%	81.4%	85.9%	89.6%	90.1%	92.7%	93.7%	95.4%
Stem Ashes of Hybiscus roja sinensis :at pH:2; Equilibration time: 2.0 hrs and sorbent concentration: 1.5 gm/lit	77.5%	90.5%	86.4%	87.6%	83.2%	90.3%	88.2%	90.0%	79.9%
Stem Ashes of Ocimum sanctu :at pH:2; Equilibration time: 2.0 hrs and sorbent concentration: 1.5 gm/lit	76.9%	87.6%	85.4%	90.8%	92.6%	94.4%	90.7%	93.8%	96.3%
Stem Ashes of Psidium :at pH:2; Equilibration time: 1.5 hrs and sorbent concentration: 1.0 gm/lit	78.1%	79.2%	86.9%	91.5%	93.4%	92.6%	91.9%	90.1%	88.0%

- 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 get sorbed by 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, these natural materials may have of metal ions like Ca, Mg, Cu, Zn, Fe, Al. and these di/trivalent metal ions form sparingly soluble salts with Chromate $^-$which 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.

- 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 [33-35] and this supports the proposed logic for the observed behavior.

- 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 (Chromate) film on the active sites of adsorbent and thus resulting in decrease in capability of the adsorbent.

- The observations made with respect to the foreign ions are also confirming as per the expected nature of extraction. % of extractability is less affected even in the presence of ten fold excess of cations chosen for study but some interference to some extent is found with some anions especially Sulphate and Phosphate.

CONCUSSIONS

1. Stem Powders and their ashes of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis, Ocimum sanctum and Psidium guajava have been found to have strong affinity towards Chromate 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 Chromate at minimum dosage and equilibration time have been optimized.
4. Sorbent dosage and time needed for the maximum removal of Chromate is less for the ashes of stems than with the raw stem powders.
5. 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. Nitrates, Chloride, Fluoride and Carbonate even when present in ten fold excess have showed marginal interference with all the bio-sorbents of the present study. Ten fold excess of Sulphates and Phosphates in few sorbents have showed interference to some extent but however, the extraction has never come down below 71.0%.
6. We claim 98.0% ,94.0%, 95.8%, 96.8%, 97.0% and 92.9 % of removal of Chromate from synthetic waters with the stem powders of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis, Ocimum sanctum and Psidium guajava respectively at pH:2 and at optimum equilibration time and optimum sorbent concentrations. The % of removal is found to be 99.9%, 98.8%, 97.3%, 98.0% , 99.0% and 99.5% in the case of stem ashes of Achyranthes aspera, Mentha, Emblica officinalis, Hybiscus roja sinensis, Ocimum sanctum and Psidium guajava respectively at pH 2 and at optimum conditions of equilibration time and sorbent concentration.
7. The suitability of the developed methodologies in this work is 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 Chromate from industrial effluents and natural lake samples as detailed in Table No:2.

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