

Received: 9<sup>th</sup> Mar-2012Revised: 18<sup>th</sup> Mar-2012Accepted: 25<sup>th</sup> Mar-2012**Research Article****NEW BIO-SORBENTS IN THE CONTROL OF CHROMIUM (VI) POLLUTION IN WASTE WATERS**

K. P.C. Sekhar, R. V. Vishnu Babu, T. Rohini, K. Ravindhranath\*

Department of Engg. Chemistry and Post Graduate Chemistry, Bapatla Engineering College, BAPATLA-422101, Guntur Dt., A.P.

\*Author for correspondence: Email: [ravindhranath.kunt@gmail.com](mailto:ravindhranath.kunt@gmail.com)

**ABSTRACT:** The sorption abilities of leaves powders of *Bhringraj*, *Aerva lanata*, *Trianthema portulacastrum* L for extracting Chromium (VI) from polluted waters have been studied with respect to various physicochemical parameters such as pH, sorption dosage and equilibrium time. The conditions for maximum removal of Chromium (VI) have been optimized. Ten fold excess of common cation ions present in natural waters, viz.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$  have synergistic effect in increasing the % removal of Chromate.  $\text{SO}_4^{2-}$  and Phosphates are found to be interfering with the extractability of Chromates but  $\text{NO}_3^-$ , Chloride, Fluoride and Carbonate have marginal interference. However, the extraction has never come down below 72.0%. Maximum extractions to an extent of 96.0%, 92.0%, and 84.0% from synthetic waters are observed with the leaves powders of *Bhringraj*, *Aerva lanata*, *Trianthema portulacastrum* L respectively at pH:2 and at optimum equilibration time and sorbent concentrations. The methodologies developed are applied to diverse waste water samples collected from industrial effluents and polluted lakes. The procedures are found to be remarkably successful in removing the Chromium(VI) from waste waters.

**Key words:** Chromium (VI), pollution control, bio-sorbents, *Bhringraj*, *Aerva lanata*, *Trianthema portulacastrum* L.

**INTRODUCTION**

The use of bio-adsorbents derived from biomaterials for the removal and accumulation of pollutants from waste waters during recent past has shown interesting results and generated the new concepts in of pollution research (Amir et al 2005; Chubar et al 2003; Dakiky et al 2002; Iqbal et al 2002; Thomas L. Eberhardt et. al., 2005, Shrihari & Raghavendra, 2003; Majeti & Kumar, 2000; Oklieimen and Onyenkpa, 1989; Orhan et al 1993, Imran Ali 2006, 2010). Bio-wastes either in their native form or chemically or thermally activated forms or both, are being investigated for their surface sorption abilities in developing simple and economically viable methods for controlling the pollutants (Oklieimen et al; 1989; Sing, D.K. et al., 2000; Shukla et al, 2002; Sandhya Babel, 2003; LezE De-bastan and Yohr Bashan, 2004; Dinesh Moham et al 2006). Further, active carbons of different plants are endowed with different surface sorption physicochemical properties and increasing research interest is being concentrated in developing new methodologies in controlling the pollutive ions using them. Imran Ali, (2010) has discussed the increasing quest for active carbon adsorbents for controlling the toxic pollutants in wastewaters. In the present work, thermally activated powders of leaves of some plants have been probed for their sorption ability towards Chromium (VI) ions from polluted waters varying various physicochemical parameters such as pH, time of equilibration and adsorbent concentration.

Chromium (VI) pollution is one of the major environmental problems due to its non-degradable nature. The salts of Chromium (VI) are used in various industries such as tanning, metallurgical, paints, inks, wood preservatives, rubber, ceramics, fungicides, photography and textile (Z Kowalski,1994; R. Negra et al , 2003; US Dept of Health & Human Services,1991; S.P.B. Kamaludee et al, 2003; E. Parameswar et al, 2009). If proper care is not devoted in the treatment and disposal methods of wastes, the problem of contamination of natural waters occurs leading to significant threat to public health (Lenore et al, 1998). As per the United Nations Food and Agriculture Organization, the maximum permissible level of Chromium for irrigation waters is 100 µg/ml and for US EPA primary drinking water standard is: 0.1 µg/ml (Lenore et al, 1998). The conventional methods based on chemical reduction, flocculation (Metcalf and Eddy, 2003), electrolysis and electroplating (S.S. Chen et al , 2007, Rajeev Upadhyay , 1992), nanofiltration (M.T. Ahamed et al , 2006) , bioaccumulation (B. Preetha et al, 2007), ion exchange (S.A. Cavaco et al, 2007), adsorption on silica composites (P.A. Kumar et al , 2007; L.T. Arenas et al, 2007), activated carbons (D. Mohan et al, 2005; Imran Ali et al , 2006), fly Ash (M. Vasanthy et al, 2004), modified zeolites (Cristian Covarrubias et al, 2005, I. Santiago et al , 1995) and bone charcoal (S. Dahbi et al, 2002, Asha Lata Singh, 2008), are expensive. They suffer from disadvantages like incomplete removal of Chromium, high reagent and energy requirements, generation of toxic sludges and further, the disposal of such sludges pose further unsustainable environmental problems. A number of patents also are existing for the removal of Chromium (US Patents).

In this contest, biosorbents are proving to be effective and economical and further, they are environmentally sustainable. Coconut fiber (G.N. Manu et al, 1997), eucalyptus bark (V. Sarin et al,2006) , maple sawdust (L.J. Yu et al, 2003), *Hevea brasiliensis* sawdust , activated carbon (P. Karthikeyan et al, 2005) , waste tealeaves and rice husk (R. Shyamala et al, 2005) , neem sawdust (V. Vinodhini et al, 2009), ficus benghalensis L.powder (L. Nageswara Rao et al 2011), marine algae *Gracilaria edulis* (S. Thilalai Natarajan, et al, 2011) and natural diatomite (Menderes Koyuncu et al, 2011), are some of the bio-sorbents investigated in controlling Chromium. Vandana Swarnkar et al (2011) studied the sorption of Chromate using HDTMA-Exchanged zeolites. Comparative studies on the removal of Chromium using different absorbents have also been made recently (A. Meena et al 2003; N.C. Kothiyal et al 2011). Asha Latha Singh reviewed the various methods available in literature in removing Chromium from wastewaters using microbes (Ashalatha Singh, 2008).

The present work is endeavored to develop simple, economical and environmentally friendly methodologies in controlling the Chromium (VI) in wastewaters evoking the sorption abilities of biomaterials derived from some plants.

## METIRIALS AND METHODS

**(A) Chemicals:** All chemicals used were of analytical grade and solutions were made with double distilled water.

1. Stock solution of Chromium (VI) having concentration 50 ppm was prepared by dissolving suitable amount of A.R. Potassium dichromate in a definite volume double distilled water. It is suitably diluted as per the need.
2. 0.25 g of Diphenyl carbazide was dissolved in 100 ml of 50% of acetone.
3. 6N Sulphuric acid solution was prepared.

**(B) Adsorbents:** Powders of Leaves of various plants were tried for the removal of Chromium (VI) 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 leaves of Bhringraj, *Aerva lanata*, *Trianthema portulacastrum* L have affinity towards the Chromium (VI) ions.

**Bhringraj****Aerva lanata*****Trianthema portulacastrum* L.****Fig : 1: Plants showing affinity towards Chromium (VI)**

Bhringraj is one of the distinguished medicinal herbs used in preparation of ayurvedic medicines especially in the treatment of hair loss, premature graying and devitalizing the hair. It belongs to Asteraceae family and it grows all over the world commonly in moist places as a weeds. *Aerva lanata* is a woody, prostrate or perennial herb belongs to Amaranthaceae family and it sometimes flowers in the first year. It grows wildly in everywhere in plains of India. Its root has a camphor like aroma, dried flowers look like soft spikes and they are sold under the commercial name : Buikallan or Boor. Its decoction of the flowers is believed traditionally to cure stones in any part of the stomach and that of the root is diuretic and cure kidney stones. *Trianthema portulacastrum* L. belongs to *Aizoaceae* family, creeps up to 800 m in sandy and muddy coastal zones of Southeast Asia, tropical America and Africa. It occurs in two biotypes: with reddish stems and green bracts. In the present study, the latter species is used. It is reported to have many therapeutic uses in curing throat ailments, Oedema, Jaundice, strangury and dropsy and also it possess hepatoprotective properties (Radanachaless T et al , 1994; Galinnato M et al, 1999)

### (C) Adsorption experiment

Batch system of extraction procedure was adopted (Gerard Kiely, 1998; Metcalf and Eddy, 2003; R.K. Trivedy, 1979). 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 (Aurthur I Vogel, 1961).

*Estimation of Chromium (VI):* An aliquot amount of Chromate sample was taken in a 50ml volumetric flask. To it, 1ml of 6N Conc. H<sub>2</sub>SO<sub>4</sub> 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. 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: 1-3 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.

**(D) 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 *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.

**(E) Applications of the developed bio-sorbents**

The adoptability of the procedures 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**

The observed sorption behavior of the adsorbents chosen for study in this work towards of Chromium (VI) with respect to various parameters such as time of equilibration, pH, sorbent dosage, interfering ions and applications are presented in the Graph No: A: 1-3; B: 1; C: 1 and Table No.:1 &2.

The following observations are significant:

1. The powders of leaves *Bhringraj*, *Aerva lanata*, *Trianthema portulacastrum* L. have been found to have affinity towards Chromium (VI) ions.
2. Percent of extractability increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability 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 *Bhringraj*, at pH: 2 and at sorption Conc. of 1.5gm/500 ml, the % of extraction is : 24.0% at 0.5 hr; 32.0% at 1.0 hr; 44.0% at 1.5 hr; 60.0% at 2.0 hr; 68.0% at 2.5 hr; 80.0% at 3.0 hr; 96.0% at 3.5 hr; 96.0% at 4.0 hr; 96.0 % at periods more than 4.0 hrs. (Vide Graph No.: A: 1). The trend is same in rest of the sorbents.
3. Effect of pH: Percentage of extraction is found to be pH sensitive. As pH decreases, percentage of extraction is found to be increasing (Vide Graph: B: 1). As for example, with the leaves powders of *Bhringraj*, % of extractability is found to be 44.0% at pH: 10, 48.0% at pH: 8, 60.0% at pH: 6, 76.0% at pH: 4 and 96.0% at pH: 2 after an equilibration time of 3.5 hrs. with sorbent concentration of 1.5 gm/500 ml. Similarly, with the leaves powders of *Aerva lanata*, % of extractability is found to be 36.0 % at pH:10, 40.0% at pH:8, 52.0% at pH:6, 64.0% at pH:4 and 92.0% at pH: 2 after an equilibration time of 2.5 hrs and with the sorbent concentration of 2.0 gm/500 ml.

In the case of leaves powders of *Trianthema portulacastrum* L. , % of extractability is found to be 20.0% at pH:10, 24 .0% at pH:8, 48 .0% at pH:6, 56 .0% at pH:4 and 84.0 % at pH:2 after an equilibration time of 2.5 hrs and sorbent concentration of 2.5 gm/ 500 ml.

- Sorbent Concentration: The sorbent dosage needed for the maximum extraction of Chromate at pH: 2 and at optimum equilibration times is found to be 1.5 gram/500 ml for the leaves powders of *Bhringraj*; 2.0 gm/500 ml for leaves powders of *Aerva lanata* ; 2.5 gm/ 500 ml for leaves powders of *Trianthema portulacastrum* L.(vide Graph No.: C:1).
- The % of maximum extractability of Chromium (VI ) at optimum conditions of pH and equilibration time are found to be 96.0%, 92.0% and 84.0% in the case of leaves powders of *Bhringraj* , *Aerva lanata*, *Trianthema portulacastrum* L. respectively (vide Graph Nos.A:1-3).
- 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.

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

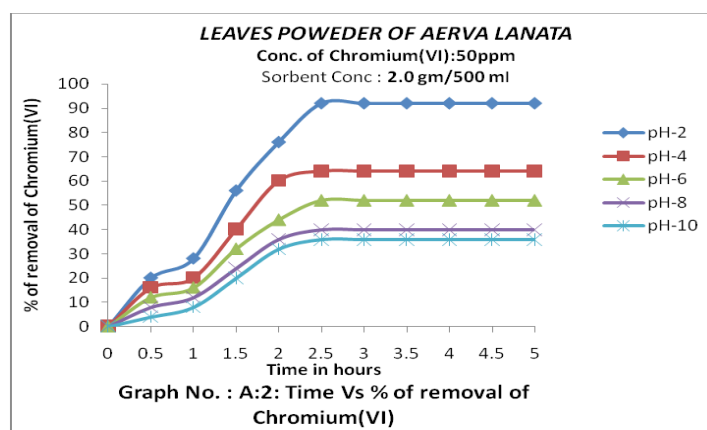
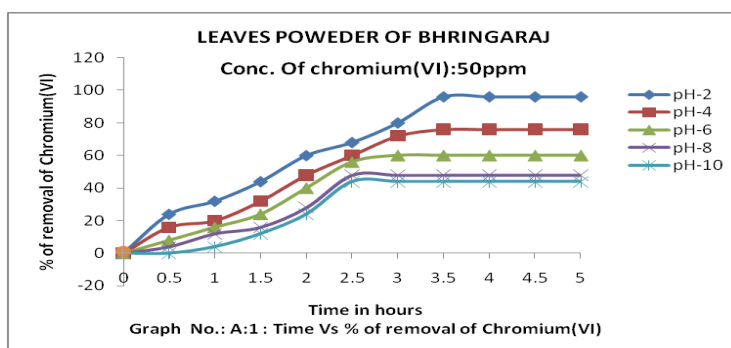
Sl.No	Interfering ions : Ten fold excess	% of maximum extractability in synthetic water samples containing 50.0 ppm of Chromium (VI)		
		<i>Bhringaraj</i> leaves Powder :mesh:75 $\mu$ pH:2 Equilibration time:3.5 hrs; Sorbent Conc.: 1.5 gms/500 ml	<i>Aerva lanat</i> leaves Powder: mesh:75 $\mu$ pH:2; Equilibration time: 2.5 hrs; Sorbent Conc.: 2.0 gms/500 ml	<i>Trianthema portulacastrum</i> L. leaves powder :mesh:75 $\mu$ pH:2; Equilibration time: 2.5 hrs; Sorbent Conc.: 2.5gms/500 ml
1	Without interfering ions:	96.0%;	92.0%	84.0%
2	$SO_4^{2-}$	88.0 %	84.3%	78.0%
3	$NO_3^{2-}$	92.2%	88.3%	83.56%
4	$Cl^-$	88.4%	88.0%	82.0%
5	$PO_4^{3-}$	84.5%	80.0%	72.0%
6	$F^-$	92.0%	84.5%	80.3%
7	$CO_3^{2-}$	96.0%	88.0%	79.5%
8	$Ca^{2+}$	96.5%	93.2%	86.1%
9	$Mg^{2+}$	97.5%	94.0%	88.8%
10	$Cu^{2+}$	98.2%	95.8%	90.5%
11	$Zn^{2+}$	97.8%	96.0%	91.5%
12	$Ni^{2+}$	98.2%	97.2%	93.8%
13	$Fe^{2+}$	98.5%	97.5%	94.1%

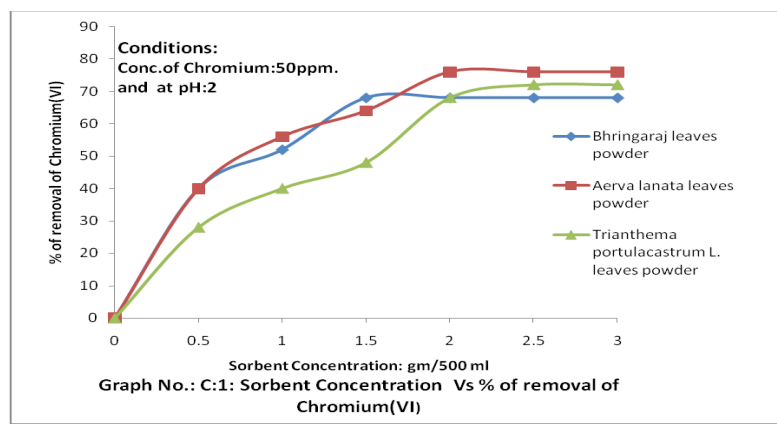
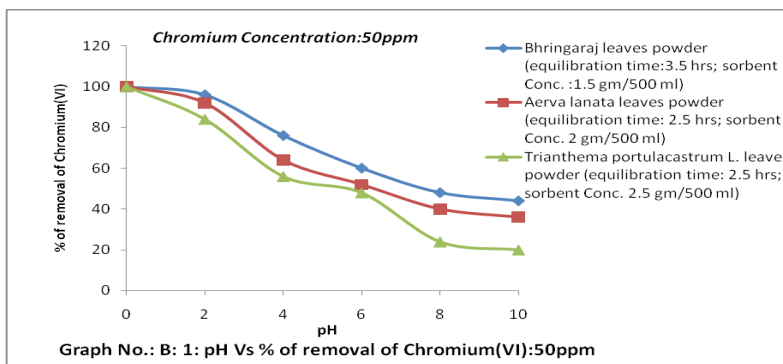
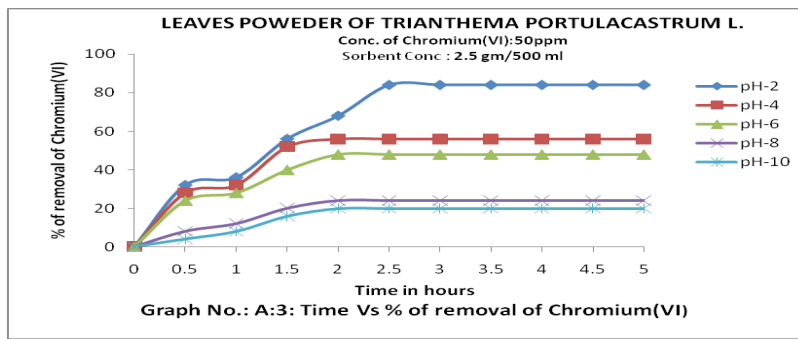
### Cations

It is interesting to note that the extractability is markedly enhanced in presence of.  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  and  $Fe^{2+}$  ions . As for example: the % of extraction is 96.0% at pH:2 with leaves powder of *Bhringraj* while in the presence of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  and  $Fe^{2+}$  ions, the % of extraction is enhanced to 96.5%, 97.5%, 98.2% and 97.8%, 98.2% and 98.5 % respectively (vide Table No.: 1:column No.3). Similarly, in the case of powders of leaves of *Aerva lanata*, the % of extraction is 92.0% at pH:2 s while in the presence of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  and  $Fe^{2+}$  ions, the % of extraction is enhanced to 93.2%, 94.0%, 95.8% 96.0%, 97.2% and 97.5% respectively (vide Table No:1: Column No. 4)). With powders of leaves of *Trianthema portulacastrum* L. , the maximum % removal of Chromium (VI) is found to be 84.0% at optimum conditions without interfering cations but in the presence of the tenfold excess of cations, the % of extraction enhanced to 86.1% for  $Ca^{2+}$ , 88.8% for  $Mg^{2+}$ , 90.5 % for  $Cu^{2+}$ , 91.5% for  $Zn^{2+}$ , 93.8% for  $Ni^{2+}$  and 94.1% for  $Fe^{2+}$  ions(vide Table No. 1: Colum No.5).

**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		
		<i>Bhringaraj leaves Powder :mesh:75 μ pH:2 Equilibration time:3.5 hrs; Sorbent Conc.: 1.5 gms/500 ml</i>	<i>Aerva lanat leaves Powder: mesh:75 μ pH:2; Equilibration time: 2.5 hrs; Sorbent Conc.: 2.0 gms/500 ml</i>	<i>Trianthema portulacastrum L. leaves powder :mesh:75 μ pH:2; Equilibration time: 2.5 hrs; Sorbent Conc.: 2.5gms/500 ml</i>
<b>Tannery Industry Effluents:</b>				
1	12.5 ppm	85.2%	84.6%	80.5%
2	21.5 ppm	89.0%	86.0%	82.0%
3	14.5 ppm	84.0%	82.5%	79.5%
<b>Chromate Plating Industry Effluents:</b>				
1	21.5 ppm	82.5%	86.5%	81.5%
2	24.5 ppm	85.5%	88.3%	79.5%
3	15.8 ppm	78.8%	81.5%	80.5%
<b>Natural Lake Samples(fed with known amounts of Chromates):</b>				
1	15.0 ppm	82.1%	89.5%	80.0%
2	20.0 ppm	84.0%	88.5%	78.5%
3	25.0 ppm	89.9%	87.0%	79.0%





**Anions**

SO<sub>4</sub><sup>2-</sup> is found to be interfering with some sorbents. % of extraction decreases from 96.0% to 88.0 % with powder of leaves of Bhringraj; 92.0% to 84.3% with leaves powder of Aerva lanata ; 84.0 % to 78.0 % with leaves powder of Trianthea portulacastrum L. (vide S. No. 2 of Table Nos:1).

Phosphate is also found to have interference with the % of extraction of Chromium (VI). The extraction reduced from 96.0% to 84.5% in the case of leaves of Bhringraj; 92.0% to 80.0% with leaves powder of Aerva lanata ; 84.0 % to 72.0 % with leaves powder of Trianthea portulacastrum L. (vide S. No. 5 of Table Nos:1).

Ten fold excess of NO<sub>3</sub><sup>-</sup>, Chloride, Fluoride and Carbonate are found to have marginal interference with the % of extractability of Chromate in all the sorbents of interest (vide Sl.Nos. 3,4,6 & 7 of Table No. 1).





It is found that the sorbents developed in this work are remarkably successful in removing Chromates in all the samples studied at optimum conditions of pH, equilibration time and sorbent dosage. as detailed in the Table 2 . Percentage removal of Chromates is found to be: 78.8% to 89.9% with leaves powder of *Bhringraj* ; 81.5% to 89.5 % with powders of leaves of *Aerva lanata*; 78.5% to 82.0% with powders of leaves of *Trianthema portulacastrum* L. (vide Table No.2).

## CONCLUSION

1. Leaves Powder of *Bhringraj* , *Aerva lanata*, *Trianthema portulacastrum* L 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. Ten fold excess of common cation ions present in natural waters, viz.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$  have synergistic effect in increasing the % removal of Chromate.
5.  $\text{SO}_4^{2-}$  and Phosphates are found to interfering with the extractability of Chromates but  $\text{NO}_3^-$  , Chloride, Fluoride and Carbonate are found to have marginal interference. However, the extraction has never come down below 72.0%.
6. We claim 96.0% , 92.0%, and 84.0% of removal of Chromate from synthetic waters with the leaves powders of *Bhringraj* , *Aerva lanata*, *Trianthema portulacastrum* L respectively at pH:2 and at optimum equilibration time and sorbent concentrations.
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 Chromate from industrial effluents and natural lake samples as detailed in Table No: 2.

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

## REFERENCES

- A. Meena and C. Rajagopal (2003). Indian Journal of Experimental Biology: 10: 72-78.
- A. Shukla, Y.H. Zhang, P. Dubdey, J.L. Margrave, and S.S. Sukla, (2002). "The role of sawdust in the removal of unwanted materials from water, J. Hazard Mater, 95: 137-152.
- Amir, Hossein Mahvi, Dariush, Naghipur, Forugh, Vaezi and shahrokh, Nazamara., (2005), "Tea waste as an adsorbent for heavy metal removal from industrial waste waters". American Journal of Applied Sciences.,2(1):372-375
- Arthur I Vogel , A Text book of Quantitative Inorganic Analysis including elementary Instrumental analysis, 3rd Edition, ELBS., 1961 792.
- Asha Lata Singh (2008). E-J of Science and Technology: 1-16.
- B. Preetha and T. Viruthagiri (2007). Biochem. Engineering J: 34 131-135.
- Chubar, Natalia, Carvalho, Jorge R. and Neiva Correia, M.J. (2003), "Cork Biomass as Biosorbent for Cu(II), Zn(II) and Ni(II)", Colloids and Surfaces A: Physicochemical and engineering aspects, 230(1-3): 57- 65.
- Cristian Covarrubias, Renan Arriagada Jorge Yanez, Rafael Garcia; Maria Angelica;, SD Barros; Pedro Arroyo and Eduardo Falabella Sousa-Aguia (2005). J of Chemical Technology and Bio-technology: 80(8) 899-908.
- D.K. Singh, and B. Srivastava, (2000). Ind. J. of Industrial Pollution Control: 16(1) 19-24.

- D. Mohan, K.P. Singh and V.K. Singh (2005). J. Chemical Technol. Biotechnol.: 44 1027-1042.
- Dinesh Mohan and Charles U. Pittman Jr. (2006). "Activated carbons and low cost adsorbents for remediation of tri and hexavalent chromium from water", J of Hazardous Materials":137(2) 762-811.
- D. Mohan, K.P. Singh and V. K. Singh (2006). J. Hazardous Materials: B135: 280-295.
- E Parameswari, A. Lakshmanan and T.Thilagavathi (2009). Australian Journal of Basic and Applied Sciences: 3 (2) 1363-1368.
- F.E. Oklieimen. and V,U. Onyenkpa, (1989). Bio Waste: 29 11
- Gerard Kiely., Environmental Engineering, McGraw-hall International Editions, 1998.
- G.N. Manju and T.S. Anirudhan, (1997). Indian J. Environ. Health: 39 289-98.
- I. Santiago, V.P. Worland, E.R. Cazes and F. Cadena,(1995). 47th Purdue Industrial Waste Conference Proceedings: 669-710.
- Imran Ali and V. K. Gupta (2006). Nature London: 1 2661-2667.
- Imran Ali, (2010). Sepn. & Purfn. Rev.,: 39 95-171.
- L. J. Yu, S. S. Shukla, K. L. Dorris, A. Shukla and J. L. Margrave (2003). J. Hazardous Materials: 100 53-63.
- L. Nageswara Rao and G. Prabhakar (2011). J. Chem. Pharm. Res, 3(6) 73-87.
- Lenore S; Clesceri, Arnold E Greenberg and Andrew D Easton (Editors), Standard Methods for the Examination of Water and Wastewater, 20th Edition, American Public Health Association, 1998, 3-65
- L.T Arenas, E.C. Lima, A.A. Santos, J.C.P. Vagheti, T. M. H. Costa and E.V. Benvenuti (2007). Colloids and Surfaces A: Physicochemical and Engineering Aspects: 297 240-248
- Luz E. De-Bastan and Yoav Bashan, (2004) "Recent advances in removing phosphorous from waste water and its future use as fertilizer (1997-2003)", Water Research, 38, pp 4222-4246, - a review article and other reference in it.
- M. Dakiky, M.Khamis, A.Manassra and M. Mereb(2002).Advances in Environ. Res : 6 533-540 .
- M. Galinnato, K.Moody and C. M. Pigginn (1999). Upland rice weeds of south and Southeast Asia IRRI. Philippines.
- M. Iqbal, A. Saeed, N.Akhtar and N. Petiolar.(2002). "Felt-sheath of palm: a new biosorbent for the removal of heavy metals from contaminated water", Bio Resource Technology: 81(2) 153-155.
- M. T. Ahmed, S. Taha, T. Chaabane, D. Akretche, R. Maachi and G. Dorange (2006). Desalination: 200 419-420 .
- M. Vasanthy, M. Sangeetha and R. Kalaiselvi, (2004). J of Industrial Pollution Control: 20 37-44.
- Menderes Koyuncu and A. Riza Kul (2011). J. Chem. Pharm. Res., : 3(1) 297-303.
- Metcalf and Eddy. (revised by George Tchobanoglous, Franklin L.Burton and H. David Stensel), Wastewater Engineering: Treatment of Reuse. 4th Edition, McGraw Hill Co., New York 2003.
- M.X. Loukidou, A.I. Zouboulis, T.D. Karapantsios and K.A. Matis (2004). Colloids and Surfaces A: Physicochemical and Engineering Aspect: 242 93-104
- N.C. Kothiyal, Deepak Pathamia and Chetan Chauhan (2011). Electronic J of Environment, Agricultural, Food Chemistry; 10(9) 2900-2912.
- N.V. Majeti, and R. Kumar, (2000). "A review of chitin and chitosan applications", React. Funct. Polym.: 46 1-27
- Orhan, Y and Buyukgungor (1993). "Removal of heavy metals by using Agricultural wastes", Water Sci. Technol. 28: 247-255
- P.A. Kumar, M. Ray and S. Chakraborty (2007). J. Hazardous Materials :143 24-32.
- R. Mehra and M. Juneja (2003). Indian Journal of Biochemistry and Biophysics: 40 131-135.
- R. Shyamala, S. Sivakamasundari and P. Lalitha (2005). J of Industrial Pollution Control: 21(1) 31-36.
- Rajeev Upadhyaya (1992). J of Indian Pollution Control: 8 81-84 .
- R.K. Trivedy (1979). Pollution Management in Industries, Environmental Publications, Karad, India .
- S. Gupta and B.V. Babu (2009). Chemical Engineering Journal : 150 352-365.
- S. Dahbi, M. Azzi, N. Saib, M De la Guardia; R. Faure and R. Durand (2002). Anal Bioanal Chem : 374 540-546 .

- Sandhya Babel and Tonni Agustions Kurniawan (2003).“Low Cost adsorbents fro heavy metals uptake from contaminated water : a review, J of hazardous materials: 97 219-243.
- S. Thillai Natarajan, R. Jayaraj, P. Jeyasingh Thanara and P. Martin Deva Prasath (2011). J. Chem. Pharm. Res. : 3(2) 595-604.
- S.A. Cavaco, S. Fernandes, M.M. Quina and L. Ferreira (2007). J. Hazardous Materials: 144 634-638 .
- S.P.B. Kamaludeen, K.R. Arunkumar;, S. Avudainayagam and K .Ramasamy( 2003). Ind. J .E. Exp. Bio: 41 972 .
- S.S. Chen, C.Y. Cheng, C.W. Li, P. H. Chai and Y.M. Chang(2007). J. Hazardous Materials: 142 362-367.
- S. Shrihari and S.K. Raghavendra (2003). Pol. Res.: 22(4) 507.
- Thomas L. Eberhardt, Soo-Hong Min James, S. Han, "Phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride" (2006),*Bioresource Technology*, 97, 2371-2376
- T. Karthikeyan;, S. Rajgopal and L. R. Miranda (2005). *J. Hazardous Materials*: B 124 192-199 .
- T. Radanachaless and J.F. Maxwell (1994). Weeds of soybean fields in Thailand. Multiple Cropping Center Publications. Thailand.
- US Department of Health and Human Services, Profile for Chromium, Public Health Service Agency for Toxic substances and Diseases , Washington, DC.,1991.
- US Patent: 3835042 (Sept 1974) 5000852 (March 1991) and 7105087 (Sept 2006); Great Britain 1394909 (Sep 1975); Switzerland: 575347 (March 1976); France:2192071 (Nov 1976);Canada: 1026472 (Feb 1978).
- V. Sarin and K. K .Pant (2006). *Bioresource Technol*: 97 15-20.
- V. Vinodhini and Nilanjana Das (2009). *American-Eurasian J of Scientific Research*: 4(4) 324-329 . ( references in it)
- Vandana Swarnkar, Nishi Agrawal and Radh Tomar (2011). *J. Chem. Pharm. Res.*: 3(3) 520—529.
- Z. Kowalski, (1994). *J. Hazardous Materials*: 37 137-144.