



## **Removal of Chromium (VI) from Polluted waters using Adsorbents derived from *Chenopodium album* and *Eclipta prostrata* Plant Materials**

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**Abstract:** The adsorption abilities of adsorbents pertaining to leaves and stems of *Chenopodium album* and *Eclipta prostrata* plants towards Chromium (VI) from polluted waters have been investigated with respect to various parameters such as equilibration time, pH and adsorbent concentration and optimized. At low pHs, the extraction is found to be more. With the sorbents derived from *Chenopodium album* plant, the % removal of Chromium (VI) is found to be 89.0% with powder of leaves (at pH:2, Eq. Time: 2.5 hrs and sorbent conc. 2.5 g/L) and 93.0% with stems powder (at pH:2, eq. time: 2.0 hrs and sorbent conc. 2.0 g/l). The maximum extraction of 92.0% is observed for leaves powder of *Eclipta prostrata* plant at pH: 2, eq. time: 3.0 hrs and sorbent conc. 3.0 g/l. With the stems powder of *Eclipta prostrata* plant, the % removal is found to be 95.0% at pH: 2, eq. time: 2.5 hrs and sorbent conc. 2.5 g/l. The extractions are not affected by co-cations generally present in the waters even when they are in 5-fold excess. Monovalent anions and carbonate have also not interfered the extraction but sulphate and phosphate ions have shown interference to some extent. The adoptability of the procedures developed in this work have been tested with respect to some industrial effluents and polluted waters and found to be remarkably successful.

**Key Words:** Chromium (VI) Pollution, Control, Bio-adsorbents, *Chenopodium album* and *Eclipta prostrata* plants, Applications.

### **Introduction**

Exploring the surface adsorption nature of bio-adsorbents derived from plant materials in controlling the potential pollutants in waters is one of the active research areas being pursued throughout the Globe [1-26]. These non-conventional methods are economical as they are based on the abundantly available raw plant materials and further, they are found to be effective and eco-friendly.

Our research group is actively investigating these methods based on bio-adsorbents and successfully developed some methodologies in removing the pollutants from waste waters (27-36). In our pilot work, *Chenopodium album* and *Eclipta prostrata* plants are found to have affinity towards Chromium (VI), a toxic ion. In the present work, bio-sorbents are prepared from these plant materials and their sorption characteristics have been optimized in evoking the physicochemical nature of the adsorbents to selectively remove Chromium (VI) from polluted waters.

The removal of Chromium ions from polluted waters assumes importance as both the trivalent and hexa-valent oxidation states are toxic and of which latter is more toxic than the former [37-42] and the

maximum permissible limit in waters is 0.05 ppm. [37-42] Chromium salts are widely used in leather, textile, paint, metallurgical, photographic, and ink industries. They are also used as wood preservatives and in the manufacture of rubber, ceramics, and fungicides [37-42]. The effluent from these industries contains substantial amounts of Chromium salts and disposal of these effluents without removing Chromium, into the natural water bodies, threatens the biota and detrimental to aquatic life and human beings.[39-42].

Conventional methods based on Chemical reduction and precipitation [41,43-45], Flocculation [43], Electrolysis and Electroplating [46,47], Nanofiltration [48], ion exchange [50] and adsorption on silica composites [51,52], and non-conventional methods based on activated carbons [1,2,53], Bioaccumulation (49), coconut fiber [5], eucalyptus bark [7], maple sawdust [8], *Hevea brasiliensis* sawdust activated carbon [9], waste tealeaves and rice husk [10] and neem sawdust [24], fly Ash [54], modified zeolites [6,55,56] and bone charcoal [57,58] have been investigated to remove Chromium from waste waters. These methods have one or the other disadvantage and the universally acceptable simple, economical, effective and eco-friendly method is still eluding the researcher.

## Materials and Methods

**(A) Chemicals:** 500 ppm stock solution of Chromium (VI) was prepared using double distilled water. 0.25% of Diphenyl carbazide in 50% of acetone and 6N H<sub>2</sub>SO<sub>4</sub> were used.

**(B) Adsorbents:** *Chenopodium album* and *Eclipta prostrata* plant materials showing affinity towards Chromium (VI) were probed in this work.



*Chenopodium album* plant



*Eclipta prostrata* plant

**Fig No. 1: Plants showing affinity towards Chromium (VI)**

*Chenopodium album* is a weedy annual plant belongs to the genus *Chenopodium* and it is also cultivated in some places and consumed in food. It grows in all soils rich in nitrogen, especially on wastelands. The leaves are un-wettable and mealy in appearance and can be used as leaf vegetable and it possesses high nutritious value. *Eclipta prostrata* is a species of plant in the sunflower family and is widespread across much of the world as a weed in warm temperate to tropical areas.

The leaves and stems of *Chenopodium album* and *Eclipta prostrata* plants were cut washed with tap water followed by distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: <75 $\mu$  and activated at 105°C in an oven and then employed in this work.

### (C) Adsorption experiment:

**Batch system of extraction procedure was adopted [43-45].**

Carefully weighted quantities of bio-adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500 ml/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 [59].

The sorption nature of the bio-sorbents towards the Chromium (VI) ions was investigated by changing continually the various physicochemical parameters such as the time of equilibration, pH and sorbent dosage. The results were presented in the **Graph Nos. A: 1-4; B: 1; and C: 1.**

#### (D) Effect of Interfering Ions:

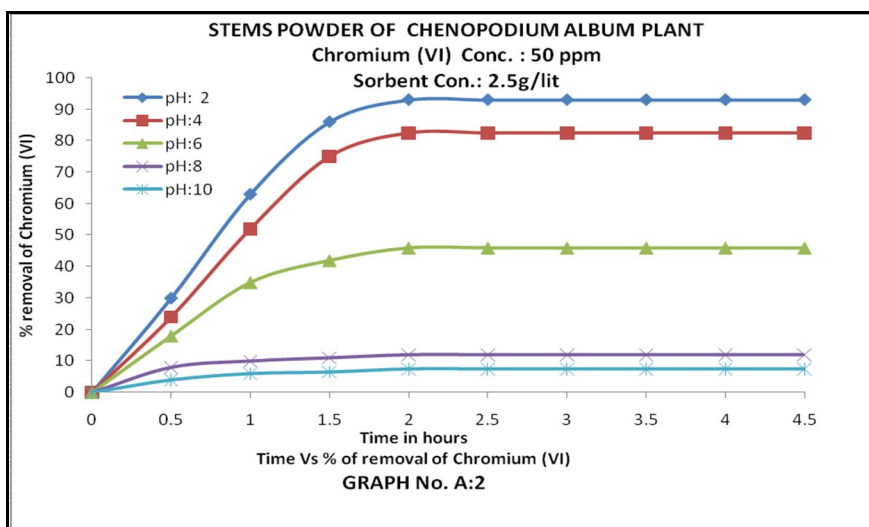
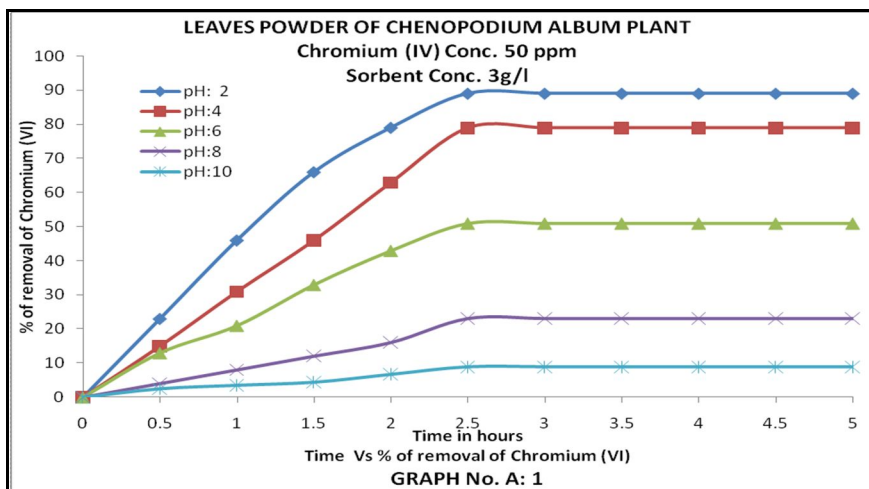
The effect of the presence of fivefold excess of co-ions commonly present in natural waters on the % of extraction of Chromium (VI) from waters was studied and the results were presented in the Table No. 1.

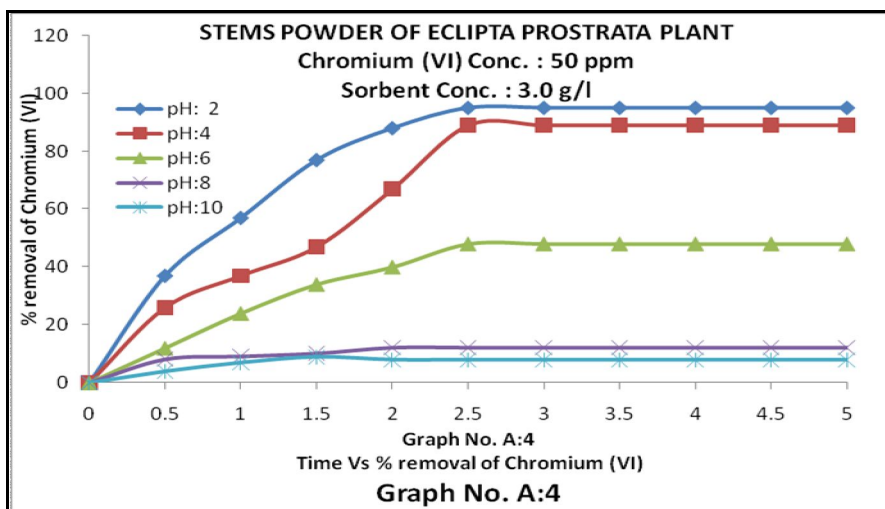
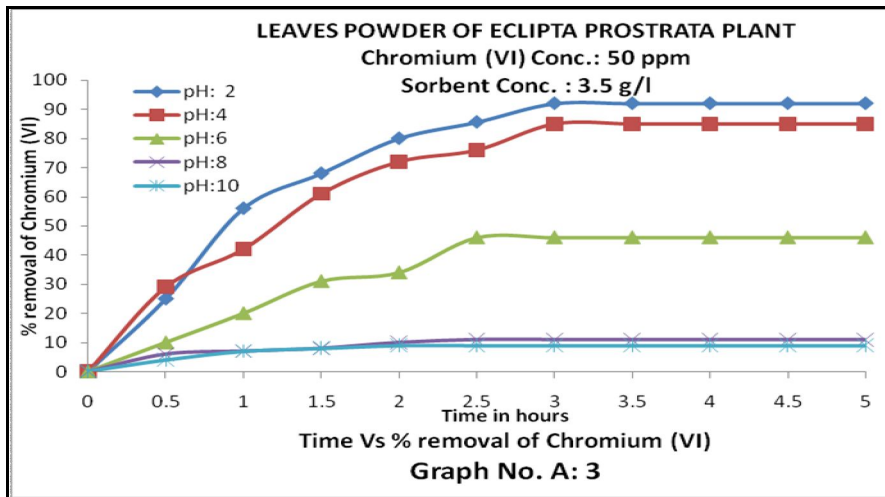
#### (E) Applications of the developed bio-sorbents:

The procedures developed in this work were applied to real samples collected from the effluents of tannery and Chrome plating industries and also from polluted lakes and their results were presented in the Table No. 2.

### Results and Discussions

The effects of various physicochemical parameters on the extraction of Chromium (VI) from waters have been studied and the obtained data is presented the Graph No. A:1-4; B:1 and C:1

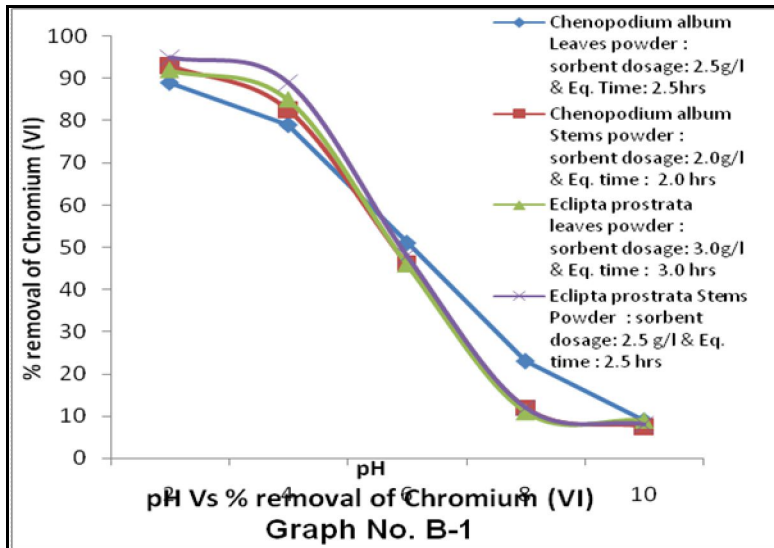




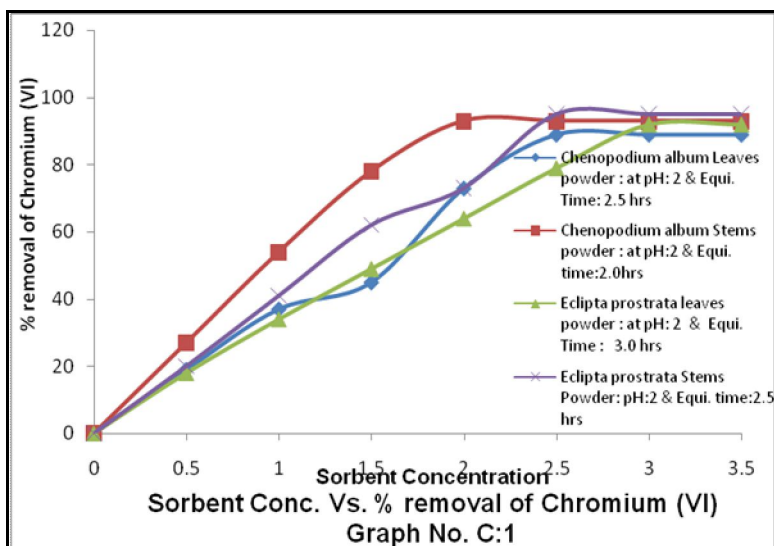
Chromium (VI) extraction is found to be effected by the extraction conditions such as pH, time allowed to equilibrate the Chromium (VI) ion solution with the adsorbent and adsorbent concentration.

pH is found to have profound influence on the extraction equilibrium. With the decrease in pH, the % removal of Chromium is found to be increasing when other extraction conditions remains constant. The % of extraction is found to be maximum at pH: 2. With the leaves powders of *Chenopodium album* as adsorbent, the % removal is found to be 89.0% at pH:2, 79.0% at pH:4, 52% at pH:6, 23.0% at pH:8 and 8.9% at pH:10 after 2.5 hrs of equilibration and with adsorbent dosage of 2.5 g/l ( vide Graph No. A: 1 and B:1) while with the stems power of the same plant as adsorbent, the % of extraction is found to be 93.0% at pH: 2, 82.5% at pH: 4, 46.0% at pH: 6, 12.0% at pH:8 and 7.5% at pH:10 after 2.0 hrs of equilibration and with 2.0 g/l of adsorbent dosage (vide Graph No. 2; B:1). With the adsorbents pertaining to *Eclipta prostrate plant*, the effect of pH on the % removal is found to be : 92.0% at pH:2, 85.0% at pH:4, 46.0% at pH:6, 11.0% at pH:8 and 9.0% at pH:10 after 3.0 hrs of equilibration and with 3.0g/l of adsorbent dosage with the leaves powders (vide Graph: A:3; B:1) and 95.0% at pH:2, 89.0% at pH:4, 48.0% at pH:6, 12.0% at pH: 8 and 8.0% at pH:10 after 2.5 hrs of equilibration time and with 2.5g/l adsorbent dosage (Vide Graph: A: 4; B:1).





The time allowed for the equilibration between the adsorbent and Chromium (VI) solution is another important factor effecting the % removal of Chromium (VI) (vide Graph No. A: 1-4). With the increase of time, the % removal is progressively increasing but after certain equilibration time, the % removal remains constant. With leaves powders of *Chenopodium album*, the % of extraction is found to be 23% at 0.5 hrs, 46.0% at 1.0 hrs, 66% at 1.5 hrs, 79.0% at 2.0 hrs, and 89.0% at 2.5 hrs or above (vide Graph No. A:1) at pH:2 and adsorbent dosage: 2.5 g/l. Similarly with the Stems powder of *Chenopodium album*, the % removal is: 30.0% at 0.5 hrs, 63.0% at 1.0 hr, 86.0% at 1.5 hrs, 93.0% at 2.0 hrs and above at pH:2 and with adsorbent dosage of 2.0 g/l (vide Graph No. A:2). The same trend is found in the case of sorbents derived from *Eclipta prostrate plant*: with leaves powders: 25% at 0.5 hrs, 56% at 1.0 hrs, 68.0% at 1.5 hrs, 80.0% at 2.0 hrs 85.6% at 2.5 hrs and 92.0% at 3.0 hrs and above (vide Graph No. A:3) (at pH:2 and with adsorbent dosage of 3.0 g/l) ; with Stems powder: 37.0% at 0.5 hrs, 57.0% at 1.0 hrs, 77.0% at 1.5 hrs, 88.0 % at 2.0 hrs, 95.0% at 2.5 hrs and above (at pH:2 and with adsorbent dosage of 2.5 hrs; vide Graph No. A:4).



The effect of sorbent dosage on the extraction of Chromium (VI) when all the other conditions remain constant has been presented in the Graph No.C:1. It is inferred from the Graph that % removal of Chromium (VI) increases with progressive increase of the adsorbent dosage. With *Chenopodium album* Leaves powder, % removal is found to be: 19% with 0.5 g/l of adsorbent, 37% with 1.0g/l, 45.0% with 1.5 g/l, 73.0% with 2.0 g/l, and 89.0% with 2.5 g/l (at pH: 2 & equi. Time: 2.5 hrs) and with stems powder of *Chenopodium album* plant, % removal is found to be: 27.0% with 0.5 g/l of adsorbent, 54.0% with 1.0 g/l, 78.0% with 1.5 g/l and 93.0% with 2.g/l (at pH: 2 & eq. time: 2.0 hrs). In the case of adsorbents derived from *Eclipta prostrate plant*, % extraction is found to be: 18.0% at 0.5 hrs, 34.0% at 1.0 hrs, 49.0% at 1.5 hrs, 64.0% at 2.0 hrs, 79.0% at 3.5 hrs and

92.0% at 3.0 hrs for leaves powder (at pH:2 & eq. time : 3.0 hrs); 20.0% at 0.5 hrs, 41.0% at 1.0 hrs, 62.0% at 1.5 hrs, 73.0% at 2.0 hrs, 95.0% at 2.5 hrs for stems powder ( at pH:2 & eq. time:2.5 hrs).

With *Chenopodium album* plant adsorbents, the maximum extraction at optimum pH: 2 are observed to be: 89.0% with leaves powders (at sorbent dosage: 2.5 gm/l & eq. time: 2.5 hrs) ; 93.0% with stems powder (at sorbent dosage: 2.0 gm/l & eq. time: 2.0 hrs). With leaves powders of *Eclipta prostrate* plant as adsorbent, the maximum possible extraction at optimum pH:2 is found to be 92.0% (with adsorbent dosage of 3.0 g/l and at eq. time of 3.0 hrs) and with the stems powder of the same plant as adsorbent, the % removal is found to be 95.0% (with 2.5 g/l of adsorbent dosage and at 2.5 hrs of eq. time).

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

Sl. No.	Interfering ions : Fivefold excess	<i>Chenopodium album plant</i> (pH/Eq. Time/Sorbent Dosage)		<i>Eclipta prostrate plant</i> (pH/Eq. Time/Sorbent Dosage)	
		<i>Leaves</i> 2 / 2.5 hrs/ 2.5 g/l	<i>Stems</i> 2/2.0 hrs/ 2.0g/l	<i>Leaves</i> 2/3.0 hrs/ 3.0 g/l	<i>Stems</i> 2/ 2.5 hrs/ 2.5 g/l
1.	Without interfering ions:	89.0	93.0	92.0	95.0
2.	$SO_4^{2-}$	65.0	68.0	70.0	74.0
3.	$NO_3^{2-}$	86.0	89.5	87.0	91.0
4.	$Cl^-$	82.0	90.0	90.0	92.5
5.	$PO_4^{3-}$	63.0	70.0	71.0	72.0
6.	$F^-$	82.0	90.0	89.0	92.0
7.	$CO_3^{2-}$	83.0	90.0	90.0	92.0
8.	$Ca^{2+}$	88.0	92.0	91.0	94.0
9.	$Mg^{2+}$	87.5	92.5	90.5	91.5
10.	$Cu^{2+}$	86.5	91.5	91.0	92.5
11.	$Zn^{2+}$	88.6	90.5	89.0	90.0
12.	$Ni^{2+}$	86.0	92.0	90.0	89.5

#### Interfering Ions:

The interference of common co-ions generally found in natural waters viz.,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $PO_3^{2-}$ ,  $Cl^-$ ,  $F^-$ ,  $CO_3^{2-}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  ions on the extraction of Chromium (VI), has been studied and the results are presented in Table No. 1. Cations, and monovalent anions:  $NO_3^-$ ,  $F^-$ , and  $Cl^-$ , have not interfered even when they are present in five fold excess. But Sulphate and Phosphate have affected the extraction to some extent.

#### Applications:

The adoptability of methodologies developed in this work have been tested by applying them to diverse samples collected from the effluents of tannery and chrome plating and also from the natural lakes (fed with known amounts of Chromate). The results are presented in the Table No: 2.

Table No: 2: Extraction of Chromium (VI) from Industrial and Natural Samples

Samples collected at different places	Cr(VI) in the Sample (found on analysis)	% of Maximum extractability			
		<i>Chenopodium album</i> plant (pH/Eq. Time/Sorbent Dosage)		<i>Eclipta prostrate</i> plant (pH/Eq. Time/Sorbent Dosage)	
		Leaves 2 / 2.5 hrs/ 2.5 g/l	Stems 2/2.0 hrs/ 2.0g/l	Leaves 2/3.0 hrs/ 3.0 g/l	Stems 2/ 2.5 hrs/ 2.5 g/l
<b>Tannery Industry Effluents:</b>					
1	20.0 ppm	87.5	92.0	91.0	94.0
2	30.5 ppm	86.5	93.0	90.0	93.0
3	26.5 ppm	85.0	91.0	89.5	92.0
<b>Chromate Plating Industry Effluents:</b>					
1	18.5 ppm	85.0	90.0	91.0	93.0
2	21.5 ppm	86.5	91.0	92.0	94.0
3	31.0 ppm	87.0	93.0	90.5	92.5
<b>Natural Lake Samples (fed with known amounts of Chromates):</b>					
1	10.0 ppm	88.0	90.0	92.0	93.0
2	15.0 ppm	86.5	91.5	91.0	90.5
3	20.0 ppm	87.0	92.5	93.0	91.5

At optimum conditions of extraction as cited in the Table No. 2, the % of extraction in the case of *Chenopodium album* plant is found to be in the range: 85.0 to 88.0% for the leaves powders and 90.0 to 93.0% for stems powders and in the case of *Eclipta prostrate plant*, 89.5 to 93.0% for leaves powders and 90.5 to 94.0% for stems powder.

### Discussions:

The bio-sorbents possesses pH sensitive –OH/-COOH groups and at high pH values, these groups dissociate to impart negative charge to surface of the adsorbent. These negative charges on the contacting surface of the sorbent, impart a kind of thrust for positively charged ions at high pH values but as the pH decreases, the dissociation of –OH/-COOH groups are less favored and at sufficiently low pH values, they would be protonated. These protonated surfaces at low pH values, develops affinity towards negatively charged ions. These tendencies of adsorption are reflected in the extraction of Chromium (VI) species.

In the pH range: 2 to 6, the Chromium (VI) presents as an equilibrium mixture of  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  and below pH:1, the predominant species is  $\text{H}_2\text{CrO}_4$ . Being anion, in the pH range studied in this work i.e. 2 to 10, it is expected to be adsorbed more when the surface groups of the sorbent are protonated (at low pH values). The pH: 2 is found to be optimum. At this pH, the species is anion and the surface is protonated and has a thrust towards the said anion. But as the solution pH increases, the de-protonation occur and subsequently, the dissociation occurs resulting the negative charge on the surface of the sorbent and thereby, not favoring the adsorption of negatively charged Chromium (VI) species.

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 inference of co-ions on the % removal is as expected: Cations and mono-valent anions are not interfering even when they are in five fold excess than the Chromium (VI) but Sulphate and Phosphate are interfering to some extent.

### Conclusions:

1. Bio-adsorbents prepared from *Chenopodium album* and *Eclipta prostrate* plant materials have been investigated for their adsorption abilities towards Chromium (VI) from simulated waters.
2. The extractions are found to be pH sensitive and the optimum pH is found to be 2. The other conditions of extraction namely, time of equilibration and adsorbent dosage have been optimized.
3. Cations and mono-valent anions have not interfered even when they are present in five fold excess than the concentration of Chromium (VI) but Sulphate and Phosphate show some interference with the extraction of Chromium (VI).
4. With simulated waters, the maximum possible extraction is found to be 89.0% and 93.0% .in the case of adsorbents derived from the leaves and stems of *Chenopodium album* plant respectively and 92.0% and 95.0% with the adsorbents pertaining to leaves and stems of *Eclipta prostrate* plant respectively.
5. The methodologies developed in this work have been successfully applied to remove Chromium (VI) from Industrial and polluted water samples. (vide Table 2)

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