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New bio-sorbents in the extraction of chromium (VI) from polluted waters

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ABSTRACT

The adsorption nature of sorbents derived from Anogeissus latifolia and Hardwickia binata have been probed for their affinity towards Chromium (VI) by changing various physicochemical parameters such as pH, time of equilibration and sorbent dosage using simulated waters and by adopting batch methods of extraction. The conditions of extraction have been optimized for the maximum removal of Chromium (VI). The extractions are found to be pH sensitive and % removal increases with decrease of pH and the optimum pH is found to 2. Equilibration time and sorbent dosage are less for sorbents pertaining to the ashes than respective powders of leaves or barks. Co-cations, univalent anions and carbonate are not interfering while Sulphate and Phosphate ions have affected the extraction of Chromium (VI) to certain extent. The methodologies developed in this work have been successfully applied to real industrial and polluted water samples.

Key words: Removal of Chromium (VI), Bio-sorption, Anogeissus latifoli, Hardwickia binata, Applications

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INDTRODUCTION

The methodologies based on bio-sorbents derived from bio-wastes in the control of pollution of natural waters, are being intensively investigated throughout the Globe [1,26]. The inherent advantages of these methods are that they are simple, economical and environmental friendly and furthermore, the raw materials are abundantly available in our surroundings.

Our research group is working on these aspects and developed methods in the control of some potential pollutants [27-36]. While we are probing the sorption nature of various bio-sorbents towards the heavy metal ions, we have noticed Anogeisus latifolia and Hardwickia binata plant materials have affinity towards Chromium (VI). In the present research work, these materials have been thoroughly probed for their inherent sorption nature and optimized conditions to evoke effective sorption nature towards the Chromium (VI) resulting the successful removal of Chromium (VI) from polluted waters.

Chromium present in both the trivalent and hexa-valent oxidation states is highly toxicity [37-42] and the maximum allowed limit is 0.05 ppm [38, 39 &42}. The main source of Chromium contamination in natural water bodies is the ill-disposing of un-treated or insufficiently treated effluents from leather, metallurgical, photographic, textile, paint, ink, wood preservatives, rubber, ceramics, and fungicides industries [37-42]. Chromium ions being non-degradable in nature get accumulated through the bio-magnifications inside the cells of living organisms and thereby detrimental to them [39-42].

Various methods based on Chemical reduction [41,43-45], Flocculation [43], Electrolysis and Electroplating [46,47], Nanofiltration [48], bioaccumulation [49], ion exchange [50], adsorption on silica composites [51,52], activated carbons [1,2,53], fly Ash [54], modified zeolites [6,55,56] and bone charcoal [57,58] have been investigated to remove Chromium salts from polluted waters. These methods have one or the other disadvantages such non-economical, tedious involving complicated procedures, less effective or less environmental friendly.

Keeping the view of the toxicity of Chromium salts and the effectiveness of bio-sorbents, investigations have been made using coconut fiber [5], eucalyptus bark [7] , maple sawdust [8], *Hevea brasilinesis* sawdust activated carbon [9] , waste tealeaves and rice husk [10] and neem sawdust [24] as bio-sorbents in the removal of Chromium ions from polluted waters. This present work is endeavored to develop, simple, economical, effective and environmental friendly procedures in this aspect of research work.

MATERIALS AND METHODS

Analytical grade chemicals were used. Potassium Dichromate 500 ppm stock solution of Chromium (VI) was prepared using double distilled water and the solution was subsequently diluted as per the need for the preparation of simulated waters. 6N H_2SO_4 and 0.25% of Diphenyl carbazide in 50% of acetone were used.

(A)Adsorbents: Anogeissus latifolia and Hardwickia binata plant materirals were probed in this work.

Anogeissus latifolia ***Hardwickia binata***

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

Anogeissus latifolia is a medium sized tree that grows up to 30 meters high and it belongs to Combretaceae family of Anogeissus genus. It is native to India and grows well in tropical conditions. The tree is leafless from Feb to May, flowering from June to September, mature fruits from December to March and leaf flushing begins in the dry season and it reaches peak before the onset of rains. This tree gives hardwood, good charcoal and gum and its leaves are used in tanning and dyeing. This is an important fodder tree for buffaloes.

Hardwickia binata is a moderate-sized tree growing from 25 to 30 m high and it belongs to monotypic genus of flowering plant in the subfamily Caesalpinioideae of the legumes. This tree grows in shallow and gravely soils and in India, it is found in western Himalayas, Central and South India especially in Kadapa, Nellore and Ceded districts and in the valleys of Cauvery and Bhavani rivers. The tree has many uses. Its bark is used for making ropes, timber is used for making agricultural equipment and its leaves, succulent stems and twigs serve as fodder for livestock.

The leaves and barks of Anogeissus latifolia and Hardwickia binata 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: <75µ and activated at 105^oC in an oven and then employed in this study. Further, these leaves and barks of the said plants were burnt to ashes and these ashes were also used in this work.

(B) Adsorption experiment:
Batch system of extraction procedure was adopted [43-45]. 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 [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: 1-8; B: 1&2; and C: 1&2.***

(C) Effect of Interfering Ions:

The effect of the presence of tenfold 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.

(D) 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 DISCUSSION

Various physicochemical parameters optimized to evoke effective sorption nature towards the Chromium (VI) have been presented in Graph No. : A-8; B: 1 & 2; C: 1&2. The salient features of the observation are:

1. pH of the solution is found to have profound influence on the sorption nature of the adsorbents. With the decrease of pH, the affinity of sorption towards Chromium (VI) increases and hence, % removal increases. For instance, with the sorbents derived from Anogeissus latifolia, % removal at pH: 2, 4, 6, 8 and 10 (and at other optimum conditions equilibration time and sorbent dosage) are found to be of respectively : 79%, 60.0%, 48.0%, 13.5% and 10.0% for the leaves powder; 89.0%, 74.0%, 53.0%, 20.1% and 12.0% for leaves ash; 85.0%, 63.0%, 42.0%, 19.0% and 12.0% for bark powders; and 94.0%, 79.0%, 64.0%, 30.0% and 20.0% for barks ashes (vide Graph No. B: 1). Similarly, with the sorbents pertain to Hardwickia binata plant, % of removal of Chromium (VI), at optimum conditions of equilibration time and sorbent concentration is found to be: 81.3% at pH: 2, 66.7% at pH:4, 50.1% at pH:6, 14.8% at pH:8; and 11.2% at pH:10 with leaves powder; 88.5%, 70.2%, 55.0%, 20.4 and 14.2% with leaves ashes; 90.0%, 69,0%, 54.0%, 18.0% and 12.0% with barks powder; and 95.0%, 72.0%, 58.0% 21.0% and 13.0% with ashes of barks (vide Graph No. B: 2).

2. The time of contact between the adsorbent and the Chromium (VI) ions solution is found to influence the % of extraction. With fixed sorbent concentration and pH, the % removal of Chromium (VI) is increased up to certain duration and after which, the % removal remains constant (vide Graph No. A: 1-8). As for example, with the leaves powders of Anogeissus latifolia plant, the % of extraction at fixed sorbent conc. 3.0 g/l and pH:2, is found to increasing : 20.0% at 0.5 hrs, 32.0 at 1.0 hrs, 43.0% at 1.5 hrs, 52.0% at 2.0 hrs, 68.0% at 2.5 hrs, 79.0% at 3.0 hrs or above (vide Graph No. A:2). The trend remains the same with all other adsorbents used in this study (vide Graph No.A:1-8). In the case of Anogeissus latifolia plant materials, the optimum periods of contact for the maximum extraction of Chromium (VI) at pH:2 and at optimum sorbent concentrations, are found to be: 3.0 hrs for leaves powder, 2.0 hrs for leaves ashes, 2.5 hrs for barks powders and 2.0 hrs for barks ash (vide Graph No. A: 1-4). With the adsorbents pertaining to Hardwickia binata plant, the optimum times needed for the maximum removal of Chromium (VI) from simulated waters at pH:2 and at optimum sorbents dosage are found to be: 3.5 hrs with leaves, 2.5 hrs with leaves ashes, 3.0 hrs with barks powder and 2.0 hrs with barks ashes (vide Graph No. A: 5-8).

3. As the sorbent dosage increases, the % removal of Chromium (VI) also increases when all other conditions of extractions are fixed (vide Graph No.C:1 & 2). The optimum sorbent dosage needed for the maximum extraction of Chromium (VI) at other optimum conditions of extraction, is found to be less for leaves and barks than with their respective ashes. As for example, with Anogeissus latifolia plant, the optimum sorbent concentration is found to be: 3.0 g/l for leaves powder and 2.5 g/l for their ashes; 2.5 g/l for barks powder and 2.0 g/l for their ashes (vide Graph No. C: 1). With the Hardwickia binata plant, the optimum sorbent dosage needed is found to be: 3.5 g/l for leaves and 2.5 g/l for their ashes; 3.0 g/l for barks powder and 2.0 g/l for their ashes (vide Graph No. C: 2).

4. With Anogeissus latifolia plant materials, the maximum possible extractions at pH: 2 are found to be: 79.0% (with sorbent dosage: 3.0 gm/l & eq. time: 3.0 hrs) with leaves powders; 89.0% (at sorbent dosage: 2.5 gm/l & eq.

time: 2.0 hrs) with ash of leave powders; 85.0% (at sorbent dosage: 2.5 g/l & eq. time: 2.5 hrs) with barks powder and 94.0% with ashes of barks (sorbent dosage: 2.0 g/l & eq. time: 2.0 hrs).

5. Interfering Ions: The effect of tenfold excess of common co-ions found in natural waters, namely, Sulphate, Nitrate, Chloride, Phosphate, Fluoride, Carbonate, Calcium, Magnesium, Copper, Zinc and Nickel ions on the % of remoal of Chromium (VI), has been studied and the results are presented in Table No. 1. It is inferred from the table that Cations and univalent anions and Carbonate have marginal effect on the % removal but Sulphate and Phosphate have to some extent affected.

Table No: 1: Effect of interfering Ions on the Extractability of Chromium 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)***							
		Anogeissus latifolia plant (pH/Eq. Time/Sorbent Dosage)				Hardwickia binata plant (pH/Eq. Time/Sorbent Dosage)			
		Leaves 2 / 3.0 hrs/ 3.0 g/l	***Leaves ash*** 2/2.0 hrs/ 2.5g/l	***Barks*** 2/2.5 hrs/ 2.5 g/l	***Barks ash*** 2/ 2.0hrs/ 2.0g/l	***Leaves*** 2/ 3.5 hrs/ 3.5 g/l	***Leaves ash*** 2/ 2.5 hrs/ 2.5 g/l	***Barks*** 2/3.0 hrs/ 3.0 g/l	***Barks ash*** 2/ 2.0hrs/ 2.0 g/l
1.	*Without interfering ions:*	79.0	89.0	85.0	94.0	81.3	88.5	90.1	95.0
2.	SO_4^{2-}	70.0	75.6	76.00	83.0	72.4	80.5	82.0	84.5
3.	NO_3^2	76.5	88.0	83.4	91.0	79.0	86.4	86.9	87.5
4.	Cl^-	75.8	87.0	84.0	90.0	80.0	85.0	85.6	88.2
5.	PO_4^3	73.0	76.5	74.0	83.0	72.5	76.5	76.0	80.0
6.	F^-	77.3	87.4	82.5	88.0	77.5	84.5	87.5	90.0
7.	CO_3^{2-}	78.7	85.6	82.0	86.5	75.0	81.4	83.9	95.6
8.	Ca^{2+}	78.0	88.0	84.0	91.0	80.0	86.7	88.0	94.0
9.	Mg^{2+}	77.5	87.5	84.2	92.0	79.7	87.5	87.0	93.0
10.	Cu^{2+}	76.7	88.0	84.5	93.0	80.5	87.0	86.9	92.0
11.	Zn^{2+}	78.6	88.5	83.6	92.5	81.0	86.5	89.0	91.0
12.	Ni^{2+}	76.0	87.5	83.5	93.5	79.0	86.0	87.5	93.5

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

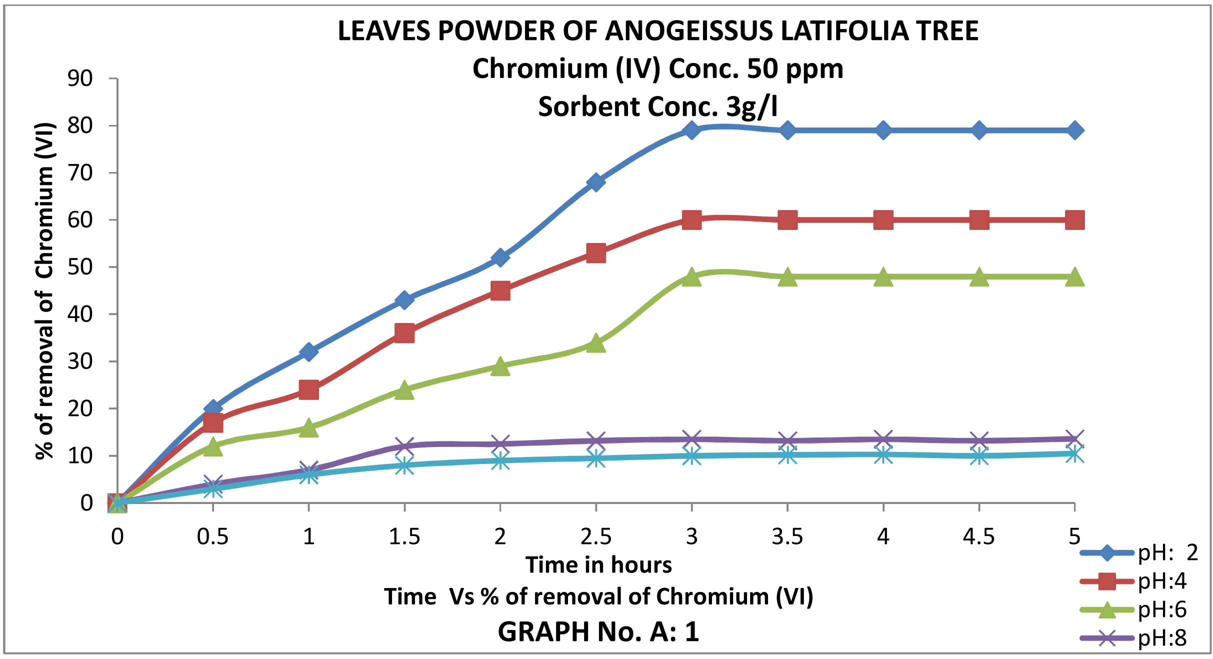
SAMPLES COLLCETED AT DIFFERENT PLACES	***Cr(VI) in the Sample (found on analysis)***	***% of Maximum extractability***							
		Anogeissus latifolia plant (pH/Eq. Time/Sorbent Dosage)				Hardwickia binata plant (pH/Eq. Time/Sorbent Dosage)			
		Leaves 2 / 3.0 hrs/ 3.0 g/l	***Leaves ash*** 2/2.0 hrs/ 2.5g/l	***Barks*** 2/2.5 hrs/ 2.5 g/l	***Barks ash*** 2/ 2.0hrs/ 2.0g/l	***Leaves*** 2/ 3.5 hrs/ 3.5 g/l	***Leaves ash*** 2/ 2.5 hrs/ 2.5 g/l	***Barks*** 2/3.0 hrs/ 3.0 g/l	***Barks ash*** 2/ 2.0 hrs/ 2.0 g/l
***Tannery Industry Effluents*:**									
1	18.0 ppm	77.5	86.5	84.0	93.0	79.0	85.5	85.0	90.2
2	24.0 ppm	76.5	84.0	83.0	92.0	80.0	84.0	84.0	91.0
3	25.5 ppm	75.0	86.0	82.5	91.0	79.5	83.0	82.5	93.0
Chromate Plating Industry Effluents:									
1	*16.8 ppm*	76.0	87.0	82.5	92.5	78.0	80.3	87.0	92.7
2	22.5 ppm	74.5	86.0	84.0	93.0	77.0	81.5	86.0	90.0
3	32.5 ppm	74.0	85.0	82.0	90.0	76.5	82.5	87.7	93.0
Natural Lake Samples*(fed with known amounts of Chromates):*									
1	*10.0 ppm*	75.8	85.0	84.0	91.3	80.0	82.0	83.4	90.0
2	15.0 ppm	73.5	86.5	82.6	92.5	79.0	83.5	86.0	92.0
3	20.0 ppm	77.0	87.5	83.0	90.6	78.1	80.0	88.0	93.1

APPLICATIONS:

The procedures developed in the work have been applied to real samples collected from the sewages/effluents of tannery and chrome plating industries and also from the natural lakes (fed with known amounts of hexavalent Chromium) and obtained results *are presented in the Table No: 2.*

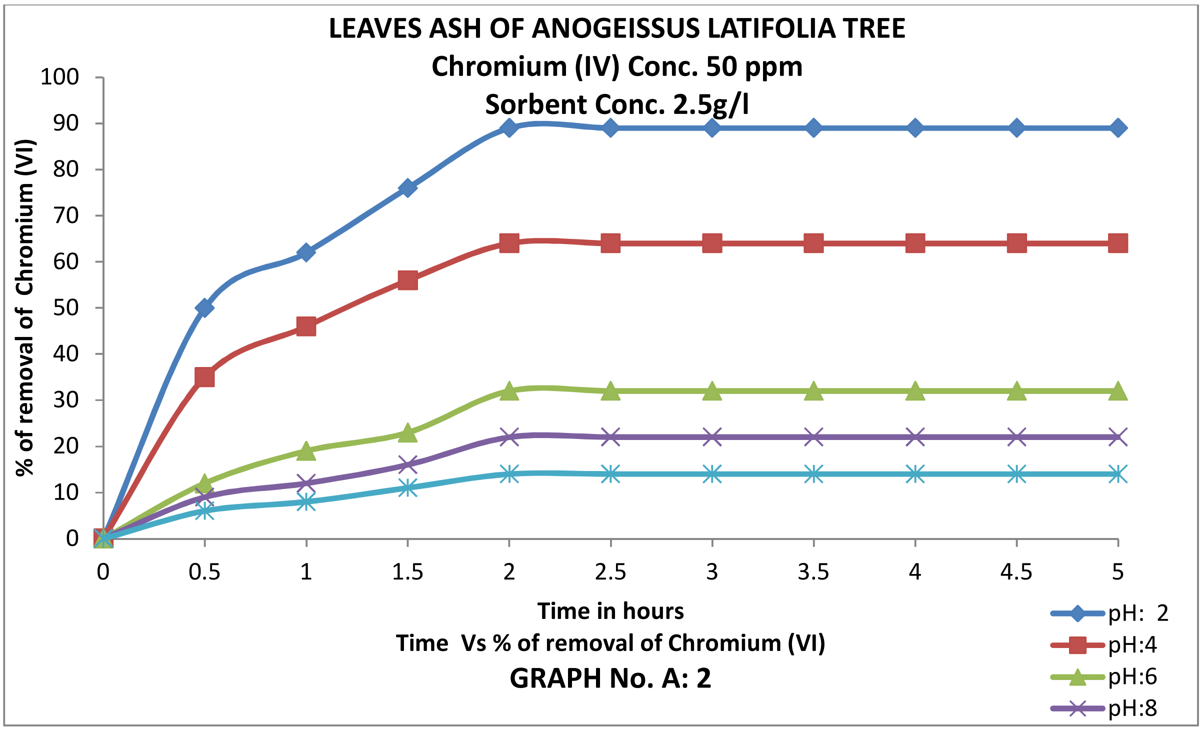
At optimum conditions of extraction as cited in the Table No. 2, the % of extraction in the case of Anogeissus latifolia plant is found to be in the range: 73.5 to 77.5% for the leaves and 84.0 to 86.5% for their ashes; 82.0 to

84.0% for barks and 90.0 to 93.0% for their ash. With Hardwickia binata plant based adsorbents, % of maximum removal at optimum conditions of extraction as given in the Table No.2 is found to be: 76.5 to 80.0% for leaves powder, 80.0 to 85.5% for the leaves ash, 82.5 to 88.0% for barks powder and 90.0 to 93.1% for the barks powder.



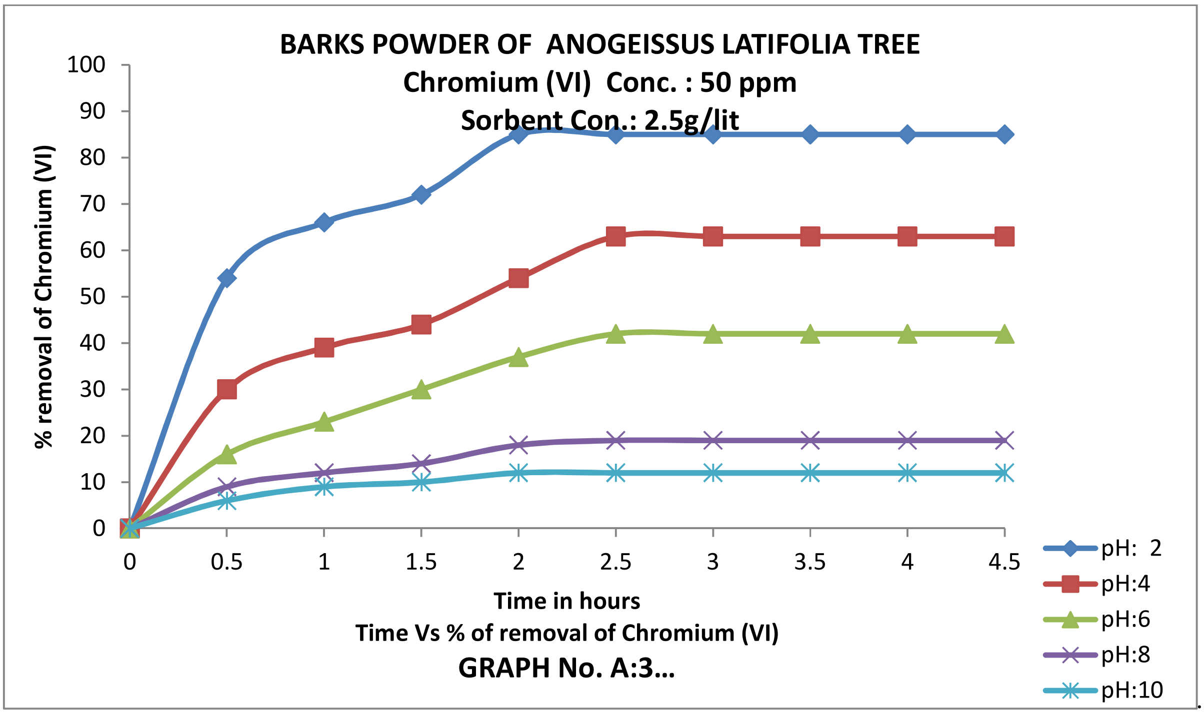
Time Vs % of removal of Chromium (VI)

GRAPH No. A: 1



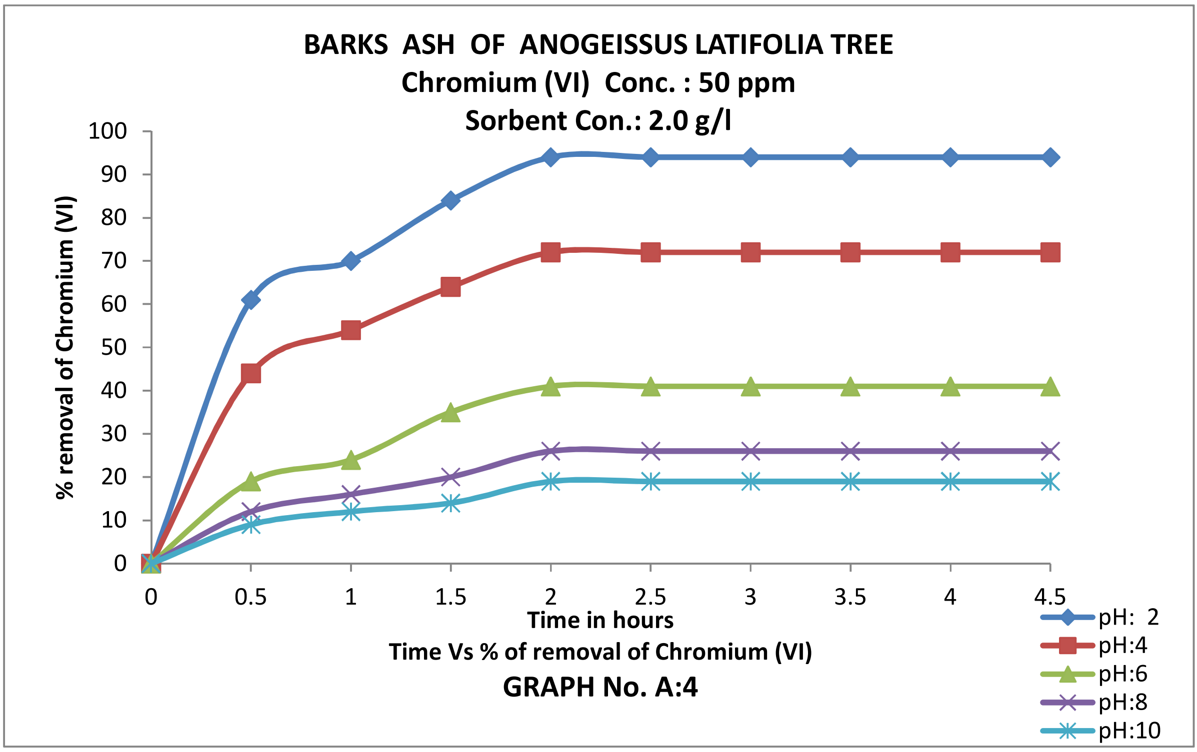
Time Vs % of removal of Chromium (VI)

GRAPH No. A: 2



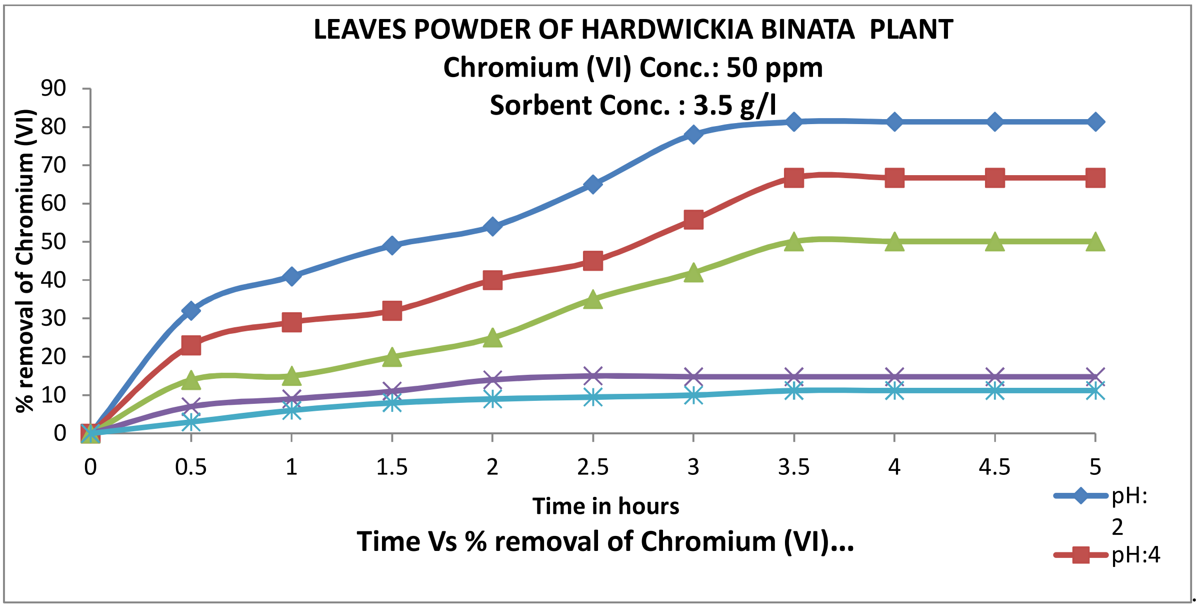
Time Vs % of removal of Chromium (VI)

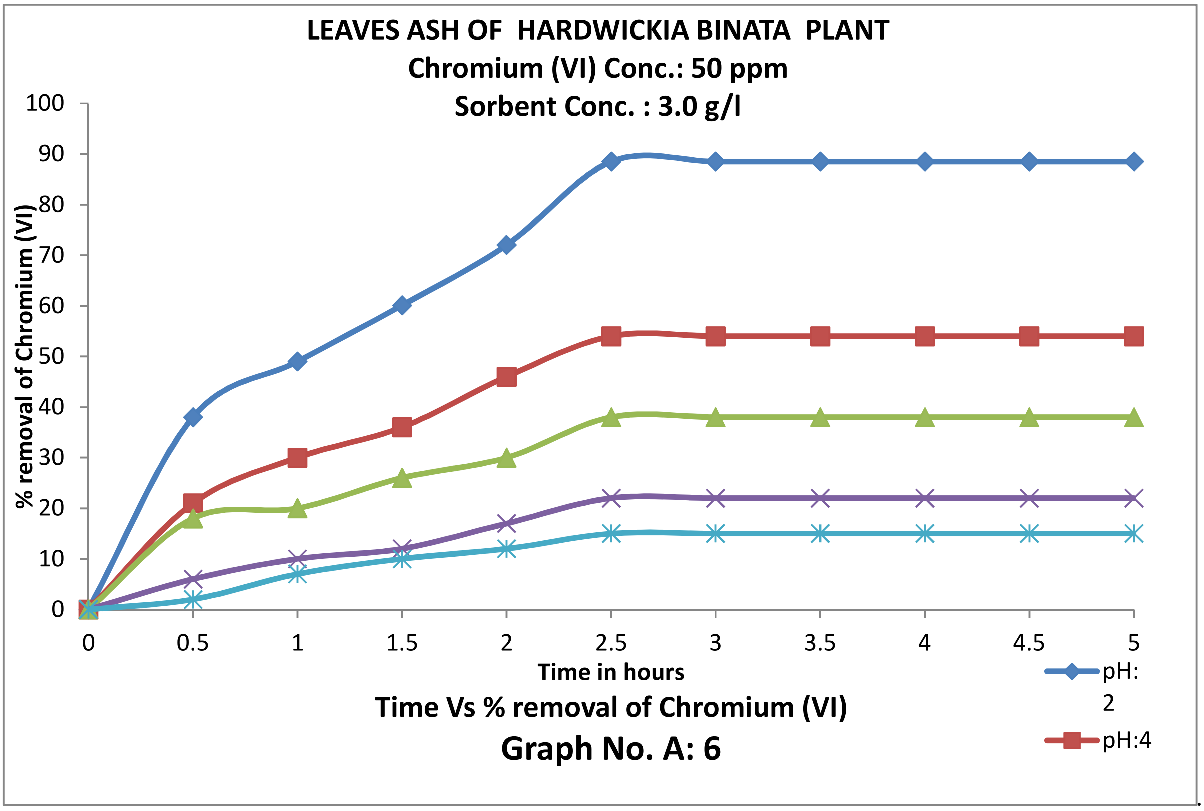
GRAPH No. A:3…



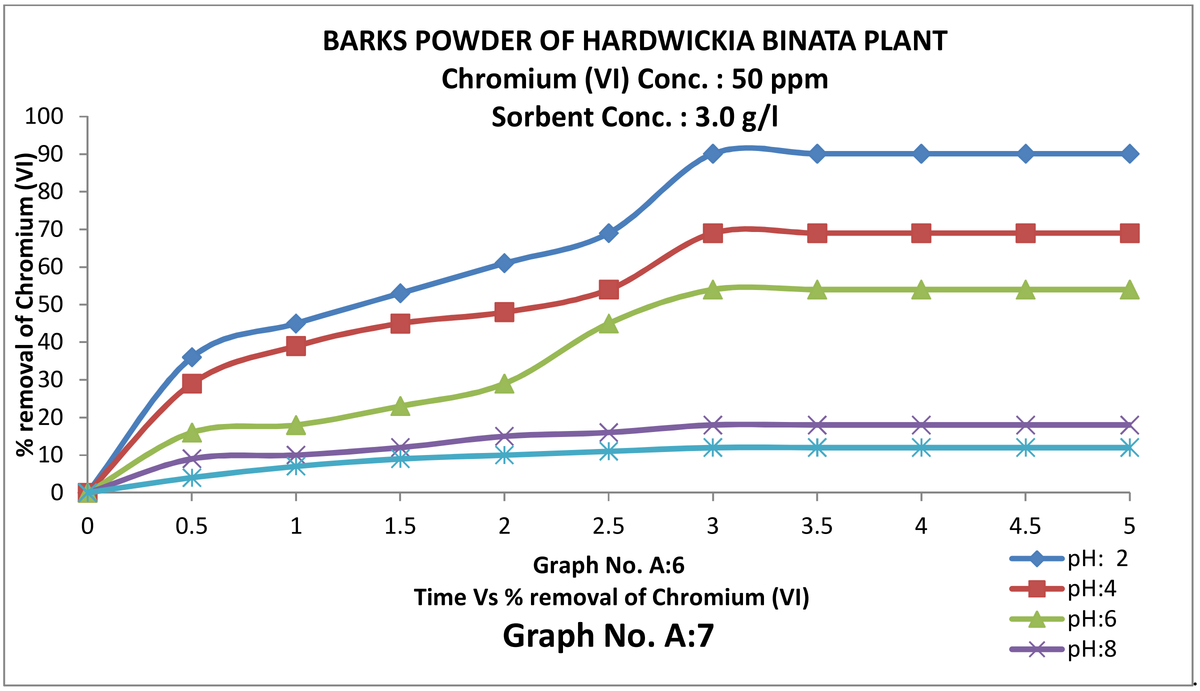
Time Vs % of removal of Chromium (VI)

GRAPH No. A:4


LEAVES POWDER OF HARDWICKIA BINATA PLANT
Chromium (VI) Conc.: 50 ppm
Sorbent Conc. : 3.5 g/l
% removal of Chromium (VI)
90
80
70
60
50
40
30
20
10
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Time in hours
Time Vs % removal of Chromium (VI)...
pH: 2
pH:4

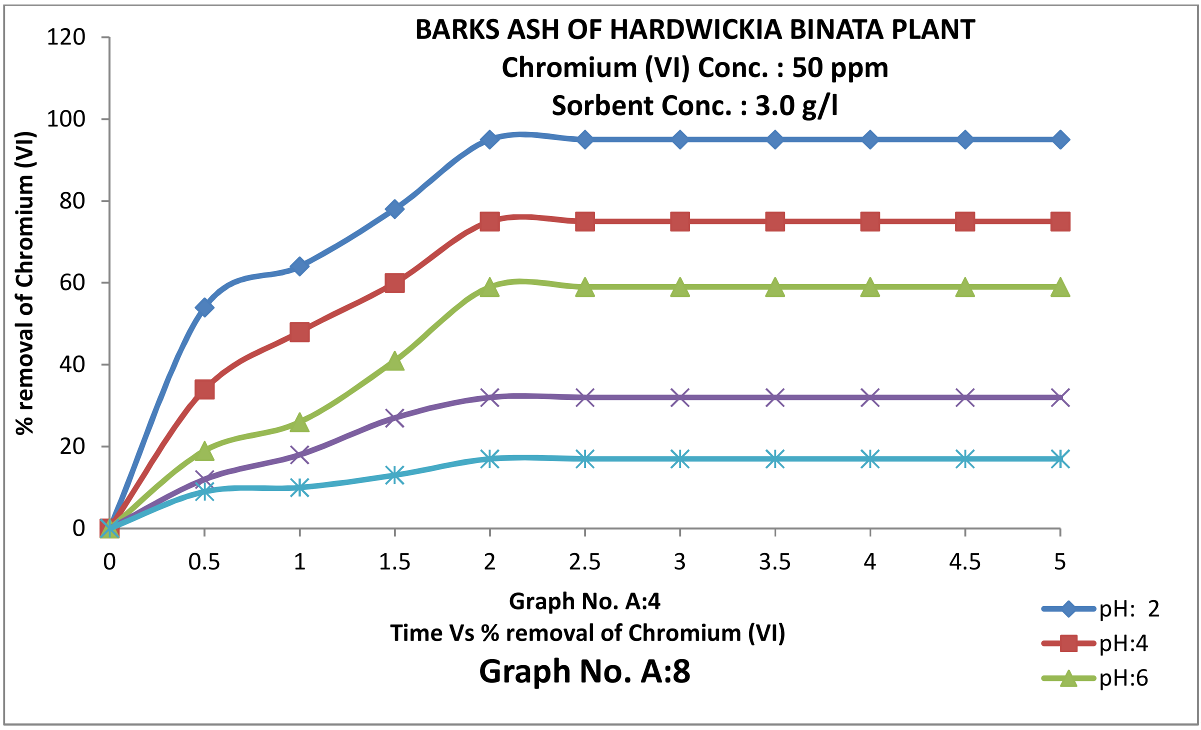

LEAVES ASH OF HARDWICKIA BINATA PLANT
Chromium (VI) Conc.: 50 ppm
Sorbent Conc. : 3.0 g/l
% removal of Chromium (VI)
100
90
80
70
60
50
40
30
20
10
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Time in hours
Time Vs % removal of Chromium (VI)
pH: 2
pH:4

Graph No. A: 6



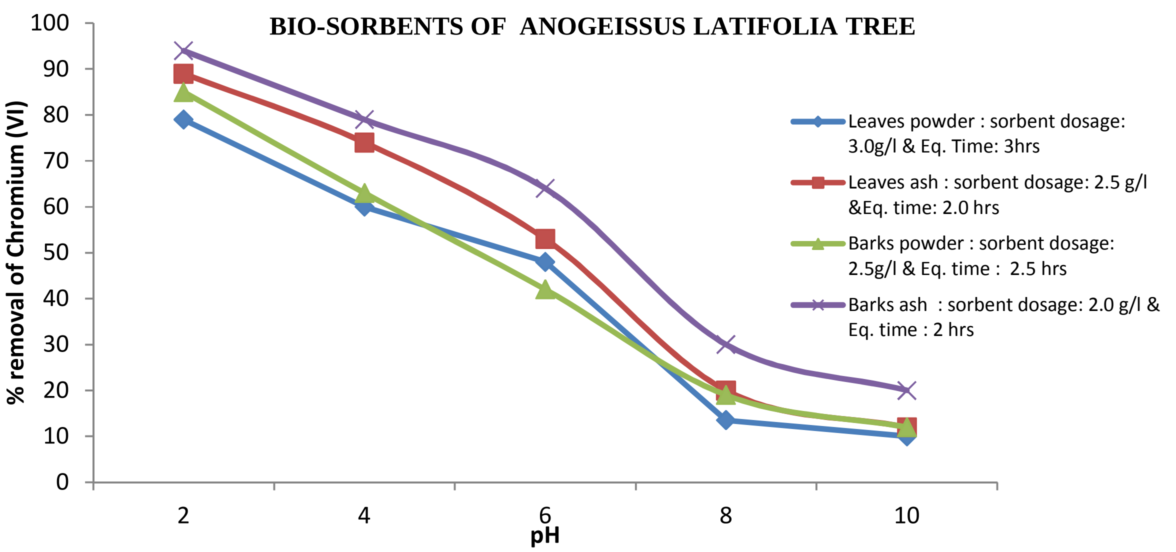
Graph No. A:6
Time Vs % removal of Chromium (VI)

Graph No. A:7



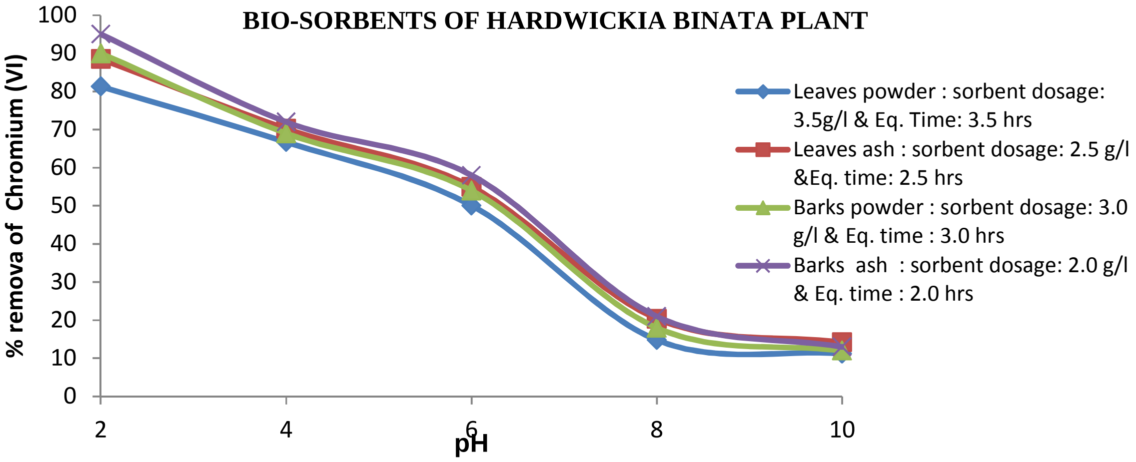
Graph No. A:4
Time Vs % removal of Chromium (VI)

Graph No. A:8



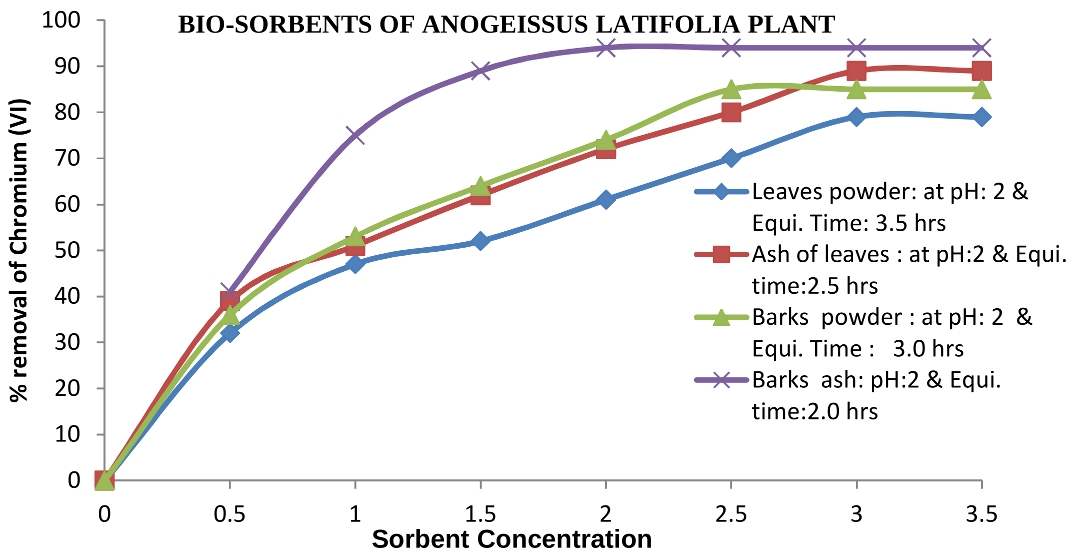
pH Vs % removal of Chromium (VI)

Graph No. B-1



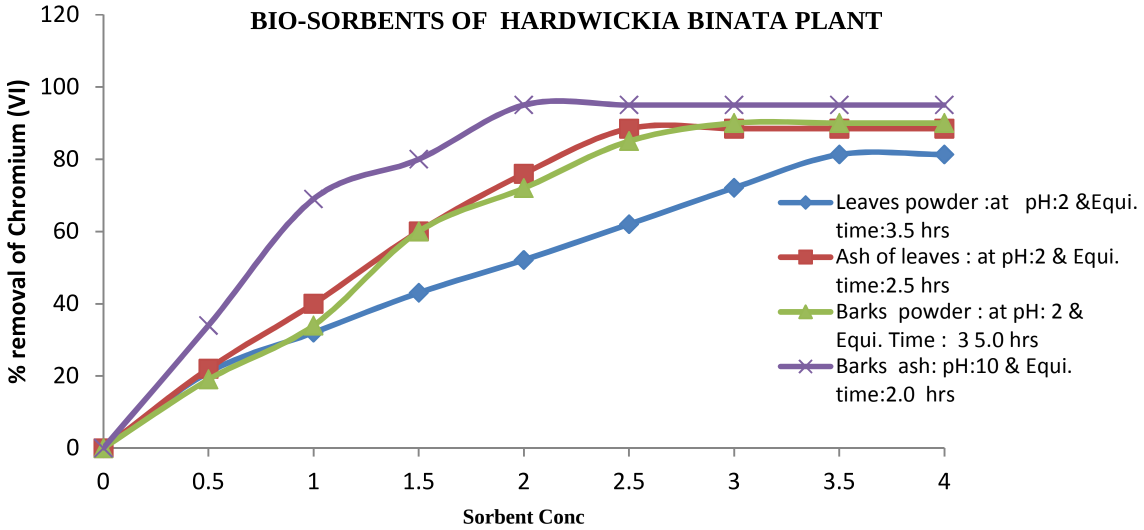
pH Vs % removal of Chromium (VI)

Graph No. B: 2



Sorbent Conc. Vs. % removal of Chromium (VI)

Graph No. C:1



Sorbent Conc. Vs. % removal of Chromium (VI)

Graph No. C:2

DISCUSSION

Bio-sorbents derived from lingo cellulosive materials possess -OH/COOH groups and these groups influence the surface sorption nature of the sorbents. These groups are sensitive to pH changes: with high pH values, the groups dissociate to yield negative charge on the surface but with low pH values, the dissociation is prevented and even protonation occurs at low pHs. This is reflected in the observed sorption nature of Chromium (VI) towards the adsorbents. The hexavalent Chromium presents as tetrahedral Chromate ions in basic solutions, as equilibrium mixture of CrO_4^{2-} and $Cr_2O_7^{2-}$ in the pH range: 2 to 6 and below pH:1, the predominant species is H_2CrO_4. In the pH range: 2-10 studied in this work, the hexavalent Chromium presents virtually as anion. Being an anion, it is adsorbed more when the surface groups are potonated at low pH values. 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 this negative charge prevailing on the interface of the sorbent does not allow the anions to be adsorbed on the surface of the sorbent. Hence, % removal is more only at low pH values and not at high pH values.

Further, the naturally present di- or trivalent impurities in sorbents derived from natural materials form sparingly metal chromates that are gelatinous in nature and are occluded in the matrixes of the sorbent enhancing the % removal of Chromium (VI).

The same explanation holds good even for ashes which too have '-OH' and '–O-' groups. 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 effect of co-ions on the % of extraction of Chromium (VI) is on expected lines: at optimum pH:2, the surface of the sorbet is charged positively and hence, Cations being positively charged are not interfering with the sorption of anionic species of Chromium (VI) on the sorbent surface at pH:2. It is interesting to note that even tenfold excess of cations are not affecting the % of extraction. Interference to some extent is noted with more profile anions like Sulphate and Phosphate and not with any univalent anions at the optimum conditions of extraction.

CONCUSSION

1. Bio-sorbents derived from Anogeisus latifolia and Hardwickia binata plant materials have been probed for their sorption characteristics towards Chromium (VI) from waste waters.
2. Various physicochemical parameters such as pH, equilibration time and sorbent concentration have been continuously varied to optimize the conditions for the maximum removal of Chromium (VI).
3. It is found that the removal is maximum at low pH: 2. The optimum adsorbent dosage and time of equilibration are found to be less for the adsorbents derived from leaves or barks than with their ashes.
4. *At the optimum condition enlisted in the Table No. 1, even tenfold excess* of co- cation ions such as , Ca^{2+}, Mg^{2+}, Cu^{2}, Zn^{2+} or Ni^{2+} have almost not effected the % removal of Chromium. Univalent ions and Carbonate have shown some marginal effect but the divalent Sulphate and trivalent Phosphate have affected the % of extraction to some extents but in any case the % of extraction has *never come down below 70.0%.*
5. We claim 79.0%, 89.0%, 85.0% and 94.0% of removal of Chromium (VI) respectively from adsorbents derived from the leaves, leaves ash, barks and barks ash pertaining to Anogeisus latifolia plant from simulated waters. In the case of Hardwickia binata plant, % of maximum removal is found to be: 81.3% for leaves powder, 88.5% for leaves ash, 90.1% for barks powder and 95.0% for ashes of bark.
6. The procedures developed have been successfully applied to real sewage samples collected from some Chromium based industries and also from the polluted lakes (fed with known amounts of Chromium (VI) (vide Table No. 2).

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REFERENCES

[1] Imran Ali and V K Gupta, *Nature, London*, **2006,** 1, 2661-2667.
[2] Imran Ali, *Sepn. & Purfn. Rev.*, **2010,** 39, 95-171.
[3] M X Loukidou, A I Zouboulis, T D Karapantsios, K A Matis, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2004,** 242, 93-104.
[4] M Dakiky, M Khamis, A Manassra, M Mereb, *Advances in Environ. Res*, **2002,** 6, 533-540.
[5] G N Manju, and T S Anirudhan, *Indian J. Environ. Health*, **1997**, 39, 289-98.
[6] D Mohan, K P Singh, V K Singh, *J. Hazardous Materials*, **2006.** B135, 280-295.
[7] V Sarin, and K K Pant, *Bioresource Technol*., **2006,** 97, 15-20.
[8] L J Yu, S S Shukla, K L Dorris, A Shukla and J L Margrave, *J. Hazardous Materials*, **2003**, 100, 53-63.
[9] T Karthikeyan, S. Rajgopal , L.R. Miranda, *J. Hazardous Materials*, **2005**, B124, 192-199.
[10] R Shyamala, S. Sivakamasundari and P. Lalitha, *J of Industrial Pollution Control*, **2005**, 21(1), 31-36.
[11] S Gupta, B V Babu, *Chemical Engineering Journal*, **2009**, 150, 352-365.

[12] S Dahbi, M Azzi, N Saib, M De la Guardia, R Faure and R Durand, *Anal Bioanal Chem* ***2002***, 374, 540-546**.**
[13] Asha Lata Singh, *E-J of Science and Technology*, 2008, 1-16**.**
[14] 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);Canda: 1026472 (Feb 1978).
[15] M X Loukidou, A I Zouboulis, T D Karapantsios, K A Matis, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2004,** 242, 93-104**.**
[16] M Dakiky, A Khamis, Manassra, Mereb, *Advances in Environ. Res*, **2002**, 6, 533-540**.**
[17] G N Manju, and T S Anirudhan, *Indian J. Environ. Health*, **1997**, 39, 289-98**.**
[18] D Mohan, K P Singh, V K Singh, *J. Hazardous Materials*, **2006**, B135, 280-295**.**
[19] V Sarin, and K K Pant, *Bioresource Technol*., **2006,** 97, 15-20.
[20] L J Yu, S S Shukla, K L Dorris, A Shukla and J L Margrave, *J. Hazardous Materials*,**2003,**100, 53-63**.**
[21] T Karthikeyan, S Rajgopal, L R Miranda, *J. Hazardous Materials*, 2005, B124, 192-199**.**
[22] R Shyamala, S Sivakamasundari, and P Lalitha, *J of Industrial Pollution Control*, **2005**, 21(1), 31-36.
[23] S Gupta, B V Babu, *Chemical Engineering Journal*, 2009**,** 150, 352-365**.**
[24] V Vinodhini, Nilanjana Das, *American-Eurasian J of Scientific Research***, 2009,** 4(4)L , 324-329 (references in it)
[25] A. Meena, and C. Rajagopal, *Indian Journal of Experimental Biology*.,**. 2003**, 10, 72-78
[26] N C Kothiyal, Deepak Pathamia and Chetan Chauhan. *Electronic J of Environment, Agricultural, Food Chemistry*, **2011**, 10(9), 2900-2912.
[27] V Hanumantha rao, Medikondu Kishore, and K Ravindhranth, *Electronic Journal of Environmental, Agricultural and Food Chemistry****, 2012, 11(5),442-*-*458.***
[28] M Divya Jyothi, K Rohini Kiran and K. Ravindhranath, *International Journal of Water Resources and Environmental Engineering***, 2012,** 4(4), 73-85.
[29] Y Hanumantharao, Medikondu Kishore, K Ravindhranath, *Journal of Analytical Science and Technology****, 2012, 3(2), 167-181***.
[30] G V Subba Rao, S Durga Rao, R Srinivasa Rao, M Appaiah and K. Ravindhranath , *Journal of Indian Water Works Association, **2012**, October-December issue.*
[31] Anna Aruna Kumari and K Ravindhranath, *International Journal of ChemTech Research*, **2012**, 4(4) 1733-174**.**
[32] O Sree Devi and K Ravindhranath, *Indian Journal of Environment Protection*, **2012**, 32(11), 943-951**.**
[33] Shaik Karimulla and K Ravindhranath, *Asian J. Research Chem***., *2012,*** 5(11), 1350 – 1359.
[34] M Suneetha, B Syama Sundar and K Ravindhranath, *Asian Journal of Water, Environment and Pollution* (IOS), **2015**, 12 (3), 33-49**.**
[35] M Suneetha, B Syama Sundar and K Ravindhranath, *International Journal of Environmental Technology and Management (INDERSCIENCE)*, **2015**, 18 (5): 420-443.
[36] M Suneetha, B Syama Sundar and K Ravindhranath, *Journal of Analytical Science and Technology*, **2015**, 6(15), 2-19**.**
[37] Z. Kowalski, *J. Hazardous Materials*, **1994**, **37**, 137-144**.**
[38] R Mehra, M. Juneja, *Indian Journal of Biochemistry and Biophysics*. **2003**, 40, 131-135.
[39] US Department of Health and Human Services, 1991, Profile for Chromium, Public Health Service Agency for Toxic substances and Diseases, Washington, D**C (1991).**
[40] S P B Kamaludeen, K R Arunkumar, S Avudainayagam and K Ramasamy, *Ind. J .E. Exp. Bio*. **2003**, 41, 972**.**
[41] E Parameswari, A Lakshmanan and T Thilagavathi *Australian Journal of Basic and Applied Sciences*, **2009,** 3 (2), 1363-1368**.**
[42] S Lenore 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**, p:3-65
[43] Metcalf and Eddy (Editor), *Wastewater Engineering: Treatment of Reuse*. 4th. Ed., McGraw Hill Co., New York **(2003).**
[44] Gerard Kiely., *Environmental Engineering*, McGraw-hall International Editions **(1998)**
[45] R K Trivedy, "Pollution Management in Industries" Environmental Publications, KARAD, INDIA **(1979).**
[46] S S Chen, C Y Cheng, C W Li, P H Chai , Y M Chang, '*J. Hazardous Materials*, **2007,** 142: 362-367**.**
[47] Rajeev Upadhyay, *J of Indian Pollution Control***,** 1992, 8, 81-84**.**
[48] M T Ahmed, S Taha, T Chaabane, D Akretche, R Maachi and G Dorange,. '*Desalination*, **2006**, 200, 419-420**.**
[49] B Preetha, T Viruthagiri, *Biochem. Engineering J*., **2007,** 34, 131-135**.**
[50] S A Cavaco, S Fernandes, M M Quina, L Ferreira, *J. Hazardous Materials*, 2007, 144, 634-638**.**
[51] P A Kumar, M Ray , S Chakraborty, *J. Hazardous Materials*,**2007**, 143, 24-32**.**

[52] L T Arenas, E C Lima, A A Santos, J C P Vaghetti, T M H Costa and E V Benvenutti, Colloids *and Surfaces A: Physicochemical and Engineering Aspects*, **2007**, 297, 240-248.

[53] D Mohan, K P Singh, V K Singh, *J.Chemical Technol. Biotechnol*., **2005**, 44, 1027-1042**.**

[54] M Vasanthy, M Sangeetha and R Kalaiselvi, *J of Industrial Pollution Control*, **2004**, 20, 37-44**.**

[55] Cristian Covarrubias, Renan Arriagada Jorge Yanez, Rafael Garcia, Maria Angelica, SD Barros, Pedro Arroyo and Euardo Falabella Sousa-Aguiar., *J of Chemical Technology and Bio-technology*, **2005,** 80(8), 899-908.

[56] I Santiago, V P Worland, E R Cazares and F Cadena, 'Adsorption of Hexavalent Chromium onto tailored zeolites', *47th Purdue Industrial Waste Conference Proceedings*, **1995,** 669-710.

[57] S Dahbi, M Azzi, N Saib, M De la Guardia, R Faure and R Durand, *Anal Bioanal Chem*, **2002,** 374, 540-546**.**

[58] Asha Lata Singh, *E-J of of Science and Technology*, **2008**, 1-16**.**

[59] Arthur I. Vogle., *A text book of Quantitative Inorganic Analysis including elementary Instrumental analysis*, **1961**, 3rd Ed., ELBS. p.792.